

1259265

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office

December 09, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

**APPLICATION NUMBER: 60/523,978
FILING DATE: November 21, 2003
RELATED PCT APPLICATION NUMBER: PCT/US04/37188**

Certified by



Jon W Dudas

Acting Under Secretary of Commerce
for Intellectual Property
and Acting Director of the U.S.
Patent and Trademark Office



BEST AVAILABLE COPY

14230 U.S. PTO

Please type a plus sign (+) inside this box → ☒

PTO/SB/16 (2-98)
Approved for use through 01/31/2001. OMB0651-0037
Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

INVENTOR(S)				
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)		
Koji	Choki	Tokyo, Japan		
Tetsuya	Mori	Tokyo, Japan		
Makoto	Fujiwara	Tokyo, Japan		
<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
OPTICAL WAVEGUIDES AND METHOD THEREOF				
Direct all correspondence to: CORRESPONDENCE ADDRESS				
<input type="checkbox"/> Customer Number		<div>Place Customer Number Bar Code Label here</div>		
OR Type Customer Number here				
<input checked="" type="checkbox"/> Firm or Individual Name	Nestor W. Shust			
Address	Hudak, Shunk & Farine Co. LPA			
Address	2020 Front St., Suite 307			
City	Cuyahoga Falls	State	OH	ZIP 44221
Country		Telephone	330-535-2220	Fax 330-535-1435
ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages	43	<input type="checkbox"/> Small Entity Statement		
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets	5	<input checked="" type="checkbox"/> Other (specify)	Express Mail Certificate	
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)				
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees				FILING FEE AMOUNT (\$)
<input type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:				160.00
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No.				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____				

Respectfully submitted,

SIGNATURE Michele M. Tympak

TYPED or PRINTED NAME Michele M. Tympak

TELEPHONE 330-535-2220

Date 11/12/03

REGISTRATION NO. 42,192

(if appropriate)
Docket Number: 203OP11211-PROV

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C., 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C., 20231.

PROVISIONAL APPLICATION COVER SHEET

Additional Page



PTO/SB/16 (2-98)

Approved for use through 01/31/2001. OMB 0651-0037

Patent and Trademark Office; U. S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection information unless it displays a valid OMB control number.

Docket Number	203OP11211	Type a plus sign (+) inside this box →	+
INVENTOR(S)/APPLICANT(S)			
Given Name (first and middle (if any))	Family or Surname	Residence (City and either State or Foreign Country)	
Yumiko	Otake	Tokyo, Japan	
Kei	Watanabe	Tokyo, Japan	
Keizo	Takahama	Tokyo, Japan	
Hirota	Nonaka	Tokyo, Japan	
Dino	Amoroso	North Royalton, OH	
Andrew	Bell	Cleveland Heights, OH	
Larry F.	Rhodes	Silver Lake, OH	
Ramakrishna	Ravikiran	Cleveland Heights, OH	

Number 1 of 1



**CERTIFICATE OF MAILING BY "EXPRESS MAIL"
UNDER 37 CFR 1.10 - SEPARATE PAPER**

Applicant: Koji Choki et al..

Serial No.:

For: "OPTICAL WAVEGUIDES AND METHOD THEREOF"

Examiner:

Group Art Unit:

"Express Mail" Label No.: EV 293764879 US

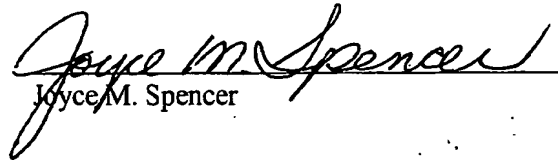
Date of Deposit: November 21, 2003

I hereby certify that this paper or fee is being deposited in the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Mail Stop Provisional Patent Application, Commissioner for Patents, Alexandria, VA 22313-1450

Respectfully submitted,

HUDAK SHUNK & FARINE CO. LPA

By:


Joyce M. Spencer

BB/jms

2020 Front Street
Suite 307
Cuyahoga Falls, OH 44221-3257
330-535-2220
Attorney Docket No.: 203OP11211

Enclosures: Return Postcard
Express Mail Certificate
Provisional Patent Application Cover Sheet (2 pgs)
Provisional Patent Application – 48 Total Pages (which includes 1 title page,
42 pages of specification and 5 pages of Drawings)
Filing Fee - Check No. 14871 in the amount of \$160.00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR PROVISIONAL PATENT

* * * * *

Optical Waveguides and Method Thereof

* * * * *

INVENTORS

Koji Choki

Tetsuya Mori

Makoto Fujiwara

Yumiko Otake

Kei Watanabe

Keizo Takahama

Hiroataka Nonaka

Dino Amoroso

Andrew Bell

Larry Rhodes

Ramakrishna Ravikiran

Optical Waveguides and Methods Thereof

TECHNICAL FIELD

[0001] The present invention relates generally optical waveguides and methods of forming them and more specifically to optical waveguides formed from polymers encompassing norbornene-type repeat units and photolithographic methods of forming such waveguides.

BACKGROUND

[0002] Data transfer using optical frequency carrier waves generated by sources such as lasers or light-emitting diodes is becoming increasingly important. One means for conducting or guiding such optical frequency carrier waves from one point to another is called an optical waveguide. Optical waveguides encompass a first medium which is essentially transparent to the light of the optical frequency carrier waves. This first medium is surrounded by, or otherwise enclosed within, a second medium having a lower refractive index than that of the first medium. Light introduced into an end of the first medium undergoes total internal reflection at the boundary with the second medium and thus guided along an axis of the first medium. Perhaps the most frequently used optical transport medium is glass formed into an elongated fiber.

[0003] However, while glass optical fibers are convenient for data transfer over long distances, they are inconvenient for complex high-density circuitry because the high density of such circuitry makes the use of glass fibers for optical interconnects problematic and expensive. Polymeric materials, on the other hand, hold great promise for constructing cost effective, reliable, passive and active integrated components capable of performing the required functions for integrated optics.

[0004] Therefore considerable effort has been directed to forming optical coupling devices and more recently to optical waveguides that can be formed of polymeric materials using photolithographic techniques. For example, in U.S. Patent No. 5,292,620, to Booth et al., waveguide structures having a predetermined geometry and a process for forming these structures using photolithographic techniques are disclosed. The structures of the '620 patent encompass at least one buried channel waveguide in a laminated matrix where the waveguide and any connecting structures are first formed in a photohardenable

film detachably disposed on a supporting substrate. After such first forming, the photohardenable film having the waveguide is detached from the supporting substrate and laminated between a first and a second photohardenable layer. In this manner, regions of the photohardenable layer adjacent the waveguide and any connecting structures serve as a cladding layer in the plane of the layer and the first and second photohardenable layers serve to clad the waveguide above and below that plane.

[0005] However, the materials disclosed in the '620 patent are acrylate type materials that have properties that are reported as making their processing very difficult (see, US Patent Application No. 20020164547 A1 to Ferm et.al.). In particular, dissolved and gaseous oxygen present within or in the proximity of the photohardenable layer can quench polymerization and therefore its abundance must be carefully regulated both within and at the immediate surface of the material. In addition, acrylate type materials, such as those of the '620 patent, are known to have relatively low glass transition temperatures which can be problematic where processing commonly used in the fabrication of microelectronic circuitry is required after waveguide fabrication.

[0006] Other polymeric materials and methods have been proposed to overcome these problems. For example, in published US Patent Application No. 20030148226 A1, to Kodama et. al., a material encompassing a (meth)acryloyloxy group-containing an organopolysiloxane resin possessing a siloxane skeleton is proposed. However, the disclosed material requires that after exposure of portions of a film formed of the material to a UV light source and curing of those exposed portions, the unexposed and hence uncured portions of the film must be dissolved away using a suitable solvent.

[0007] Therefore it would be advantageous to provide a polymeric material useful for forming optical waveguides that does not encompass acrylate type materials and the difficult processing the use of such materials requires. In addition, it would be advantageous to provide such polymeric materials and methods where forming optical waveguides therein, do not require removing some of the material to define the waveguide channels or cores. Also it would be advantageous to provide polymeric materials and methods useful for forming optical channels and cores having low propagation losses.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Embodiments of the invention are described below with reference to the following accompanying drawings.

[0009] Figs. 1, 2 and 3 are schematic drawings that illustrate in a simplified manner a sequence of forming waveguide regions in a waveguide patternable film in accordance with an exemplary embodiment of the present invention;

[0010] Fig. 4 is an Electron Probe Microanalysis (EPMA) of a structure formed in the manner of the sequence depicted in Figs. 1, 2 and 3;

[0011] Figs. 5, 6, 7, 8 and 9 are schematic drawings that illustrate in a simplified manner a sequence of forming waveguide regions in a waveguide patternable film in accordance with another exemplary embodiment of the present invention; and

[0012] Fig. 10 is a bar chart depicting the amount of energy output by a typical mercury vapor lamp at selected wavelengths within the UV spectrum and an overlaid absorption spectra of RHODORSIL® PHOTOINITIATOR 2074 (available from Rhodia USA Inc., Cranbury, NJ).

DETAILED DESCRIPTION

[0013] Exemplary embodiments in accordance with the present invention will be described. Various modifications, adaptations or variations of such exemplary embodiments described herein may become apparent to those skilled in the art as such are disclosed. It will be understood that all such modifications, adaptations or variations that rely upon the teachings of the present invention, and through which these teachings have advanced the art, are considered to be within the scope and spirit of the present invention.

[0014] The term "norbornene-type" is used herein to mean a monomer material that contains at least one norbornene moiety in accordance with Structure A shown below, or a polymeric material that was formed from such monomers and that has at least one repeat unit in accordance with Structure B, also shown below.:



[0015] The terms "crosslinker" and "crosslinking monomer" are used interchangeably herein to mean a monomer that contains at least two norbornene-type moieties such as shown above by 'A', each being polymerizable. Such crosslinkers include both fused multicyclic ring systems and linked multicyclic ring systems, as will be described more fully below.

[0016] The terms waveguide channel or core refer to a portion of a polymeric film having a square or rectangular cross-sectional profile with the dimensions of the square or rectangular cross-sectional profile ranging from about 1 μ m to about 200 μ m in some embodiments, from about 5 μ m to about 100 μ m in other embodiments and from about 10 μ m to about 60 μ m in still other embodiments. Such waveguide channel or core regions are further characterized as having a refractive index that is higher than the refractive index of laterally adjacent regions which are referred to as cladding regions.

[0017] Referring first to Fig. 1, a portion of a waveguide patternable film 10 of a photo-induced thermally developable material (PITDM), in accordance with embodiments of the present invention, is depicted disposed on a support substrate 5. Generally, substrate 5 is a silicon, silicondioxide, glass or quartz substrate, or a polyethylene terephthalate (PET) film.

[0018] The PITDM encompasses a norbornene-type polymeric material matrix 15 having a plurality of norbornene-type repeat units and materials 20 dispersed therein to form a varnish solution of such materials 20 and matrix 15. Materials 20 include a cationic photoinitiator material, a procatalyst material and a norbornene-type monomer material. Generally, the PITDM of film 10 also encompasses one or more antioxidant materials to prevent undesirable free radical generation and autooxidation of the norbornene-type materials, although the inclusion of such antioxidants can be optional where the PITDM is not subjected to oxidative conditions or where the period of such exposure is limited. Each of the materials 20 is essentially uniformly and randomly distributed within matrix 15, thus when film 10 is formed, such materials 20 are essentially uniformly and randomly distributed therein.

[0019] The PITDM is applied to substrate 5 to form film 10 using any one of several appropriate application methods. Such methods include, but are not limited to, spin coating, spray coating, dip coating and spreading with a doctor blade. In one exemplary embodiment of the present invention, a solution of the PITDM, also referred to herein as a "varnish solution," is poured onto a glass

substrate and spread to an essentially uniform thickness using a doctor blade. In some embodiments of the present invention, the essentially uniform thickness is from about 5 μ m to about 200 μ m, while in other embodiments layer 10 has a thickness of from about 10 μ m to about 100 μ m and in still other embodiments layer 10 has a thickness of from about 15 μ m to about 65 μ m. After spreading, the coated glass substrate is allowed to sit on a vented leveling table to allow the spread film to level surface irregularities resulting from the method of application as well as to allow for solvent evaporation and the forming of a solid film, such as PITDM film 10 depicted in Fig. 1. It will be noted that PITDM film 10 is created by spreading the varnish solution to an essentially uniform thickness, materials 20 and matrix 15 encompassed within such varnish solution are essentially uniformly and randomly distributed within film 10 disposed on substrate 5.

[0020] Matrix 15 generally encompasses a norbornene-type polymer having two or more distinct norbornene-type repeat units. For example, the polymer resulting from the polymerization of essentially equal amounts of hexylnorbornene (HxNB) and diphenylmethyl norbornenemethoxysilane (diPhNB) results in a copolymer that is useful for matrix 15. However, it will be noted that while matrix 15 generally encompasses two or more distinct norbornene-type repeat units, the inventors believe that for some embodiments in accordance with the present invention, matrix 15 can be an appropriate homopolymer. Hence such appropriate norbornene-type homopolymers are within the scope and spirit of the present invention.

[0021] Materials 20 include one or more distinct norbornene-type monomers where at least one of such monomers is a crosslinking norbornene-type monomer. An exemplary crosslinker and norbornene-type monomer found useful for embodiments of the present invention as bis-(norbornenemethoxy) dimethylsilane (SiX), and hexyl norbornene (HxNB), respectively:

[0022] Cationic photoinitiators, in accordance with the present invention, are generally commercially available materials that decompose upon exposure to actinic radiation of an appropriate wavelength to form, in pertinent part, a cation such as a proton, and a weakly coordinating anion (WCA) such as tetrakis(pentafluorophenyl)borate, tetrakis(pentafluorophenyl)gallate, aluminates, antimonates, other borates, gallates, carboranes and halocarboranes. Exemplary materials useful in embodiments of the present invention RHODORSIL®

PHOTOINITIATOR 2074 ((tolycumyl) iodonium tetrakis (pentafluorophenyl) borate, CAS No. 178233-72-2), available from Rhodia USA Inc., Cranbury, NJ and TAG-372R photo acid generator (dimethyl (2-(2-naphthyl)-2-oxoethyl) sulfonium tetrakis (pentafluorophenyl) borate, CAS No. 193957-54-9) available from Toyo Ink Mfg. Co., Ltd. of Tokyo, Japan.

[0023] Procatalysts of the present invention generally encompass molecules represented by formula I:



where $(R)_3E$ represents a Group 15 neutral electron donor ligand wherein E is an element selected from Group 15 of the Periodic Table of the Elements, R independently represents hydrogen or a hydrocarbyl containing moiety, and Q is an anionic ligand selected from a carboxylate, thiocarboxylate, and dithiocarboxylate group. One such exemplary procatalyst is $Pd(PCy_3)_2(OAc)_2$ (Pd785) where Cy is an abbreviation representing a cyclohexyl moiety and Ac is an abbreviation representing an acetate moiety.

[0024] Where antioxidants are included in materials 20, Ciba® IRGANOX® 1076 and Ciba® IRGAFOS® 168, available from Ciba Specialty Chemicals Corporation, Tarrytown, NY., have been found useful, although other appropriate antioxidants can also be used. Some other exemplary antioxidant include Ciba® Irganox® 129, Ciba® Irganox® 1330, Ciba® Irganox® 1010, Ciba® Cyanox® 1790, Ciba® Irganox® 3114 and Ciba® Irganox® 3125.

[0025] Turning now to Fig. 2, the portion of spread film 10 shown has been dried, that is to say that essentially all of any solvent(s) used to form a solution of matrix 15 and materials 20 have been allowed to evaporate and a solid spread film 10 is formed. Solid spread film 10 of the PITDM has a first Refractive Index (RI) through out where such first RI is a function of the materials selected for matrix 15 and uniformly dispersed materials 20 therein.

[0026] As depicted, regions 25 of film 10 are exposed to actinic radiation 30 through masking element 35, where a source of actinic radiation 30 is selected based on the sensitivity of the cationic photoinitiator in materials 20 to such radiation. Thus, where RHODORSIL® 2074 is employed in film 10, a mercury vapor lamp is used as an ultraviolet (UV) radiation source to provide sufficient energy below 300 nanometers (nm) to cause the decomposition of the Rhodorsil and provide the cation and WCA as mentioned above. Laterally adjacent to

exposed regions 25 are unexposed regions 40 which are protected from radiation 40 by opaque portions of masking element 35 as depicted.

[0027] It will also be understood that while masking element 35 is depicted as only having two openings for allowing radiation 30 to pass through to regions 25 of film 10; such a depiction is simplified, and masking element 35 can be provided having a variety of more complex patterns to define one or more optical waveguide elements and/or coupling devices. For example, waveguides in accordance with embodiments of the present invention can be used for data communication applications such as "On board Chip to Chip Interconnects;" Optical Switches; and a variety of optical backplane applications such as Optical Add Drop Multiplexers (OADM); Multiplexers and Demultiplexers; Arrayed Waveguide Gratings (AWG); Microelectro-mechanical Systems (MEMS) and Microoptoelectro-mechanical Systems (MOEMS). In addition, fabrication methods in accordance with the present invention are useful to form diffraction gratings and holographic film. Thus it will be realized that the types of waveguide structures that can be made using the methods of the present invention are generally limited only by the availability of a photomask having the pattern required by the application. However, regardless of the complexity of any pattern used to define optical waveguide elements, each exposed region 25 defined by such pattern will have one or more unexposed regions 40 laterally adjacent thereto.

[0028] Without wishing to be bound by theory of invention, it is believed that upon exposure to radiation 30, the photoinitiator in exposed regions 25 reacts or decomposes, in response to the exposure, to release a proton, or other cation, and a weakly coordinating anion (WCA). The proton and WCA serve to cause the forming of an active but latent catalyst *in situ*, that is to say within exposed regions 25 of film 10. It will be understood that referring to the catalyst as "active but latent" means that absent any additional changes/reactions, such latent catalyst will not cause the polymerization of the norbornene-type monomers within regions 25 at room temperature.

[0029] Turning to Fig. 3, the structure of Fig. 2 is shown after thermal curing. That is to say, the structure of Fig. 2 is heated to a first temperature for a first period of time and then to a second temperature, higher than the first, for a second period of time. The first temperature is sufficient to cause the latent catalyst to become an active catalyst and cause polymerization of the norbornene-type monomers within regions 25. Advantageously, it has been found that in addition to the polymerization of the norbornene-type monomers originally dispersed within

regions 25 at the time of the exposure to actinic radiation 30, additional norbornene-type monomers diffuse into exposed regions 25 from contiguous, unexposed areas of film 10 and are polymerized therein.

[0030] Before any exposure to actinic radiation 30, PITDM film 10 has a first refractive Index (RI). After such exposure and subsequent curing, exposed regions 25 have a second RI and laterally adjacent unexposed regions 40 have a third RI, where each of the second RI and the third RI is different from each other and from first RI. As mentioned above, the norbornene-type monomers employed in embodiments of the present invention are selected such that when they are polymerized within exposed regions 25, the resultant polymer changes the RI of such exposed regions 25 from the first RI to the second RI. In addition, it has been found that norbornene-type monomers from unexposed regions 40 diffuse into exposed regions 25 and are polymerized therein. Such diffusion of monomers from unexposed regions 40 to exposed regions 25 changes the RI of regions 40 from the first RI to the third RI.

[0031] Where the second RI of exposed regions 25 is lower than the third RI of unexposed regions 40, such unexposed regions 40 serve as optical waveguide cores or channels and exposed regions 25 serve as laterally adjacent cladding regions. Alternatively, where the second RI is higher than the third RI, exposed regions 25 serve as optical waveguide cores or channels and the unexposed regions 40 serve as laterally adjacent cladding regions.

[0032] It should be noted that the thermal curing described briefly above is particularly advantageous when the first period of time is sufficient for polymerization within regions 25 to be substantially complete to make the pattern of waveguide channel and clad regions visible. In addition, it is advantageous for the second temperature to be sufficiently high to cause any remaining cationic photoinitiator to thermally decompose and form the same species as previously described being caused by radiation 30. It is believed, again without wishing to be bound by theory of invention, that this second heating results not only in the polymerization of any residual, not yet polymerized, norbornene-type monomers within exposed regions 25, but also to cause the polymerization of any of such monomers remaining in unexposed regions 40. In this manner, heating to the second temperature serves to stabilize the resulting structure of optical waveguide channel (or core) having laterally adjacent cladding regions.

[0033] In addition to this at least two step curing cycle, it has been found advantageous wait for a period of time of about 30 minutes to about 60 minutes

before beginning the first step of the thermal cure cycle of an exposed structure. While it is uncertain why this waiting period is advantageous, it is possible that due to the very low rate of diffusion or propagation at room temperature, delaying the thermal cure may allow for a more complete or uniform conversion of procatalyst to latent catalyst thus providing for more uniform polymerization within the exposed region.

[0034] Referring to Fig. 4, an Electron Probe Microanalysis (EPMA) of a waveguide pattern formed in a waveguide patternable film in accordance with the process steps described above (see, Example 2, below). For the purpose of enhancing the sensitivity of the EPMA only, the plurality of norbornene-type monomers used for forming the waveguide pattern used for the EPMA of Fig. 4, only consisted of the crosslinker monomer SiX. In this manner, the concentration of silicon available for detection by the analysis instrument was increased. Focusing on the upper portion of the EPMA where silicon concentration is mapped, it is readily evident that in each of the narrow vertical regions (unexposed), the silicon concentration is greatly reduced relative to the adjacent regions (exposed). It is believed that such an EPMA is indicative of the diffusion of SiX monomer molecules from unexposed regions into exposed regions wherein a homopolymer is formed by the action of the catalyst formed therein.

[0035] It will be understood that the description of the structures depicted in Figs. 1, 2 and 3 as well as the description of the processing applied to each of such structures, shows the formation of optical waveguide regions within waveguide patternable film 10. It will be noted, however, that additional processing of the film containing the optical waveguides is contemplated. For example, in some embodiments of the present invention, after forming the optical waveguides, it is contemplated that film 10 will be removed from substrate 5 and laminated to or otherwise disposed on and affixed to other layers that will serve as cladding for the core surfaces having laterally adjacent cladding regions. Such cladding layers are selected or formed to have a refractive index (RI) similar to the RI of the laterally adjacent cladding regions formed in film 10.

[0036] In Figs. 5-9 a sequence of forming waveguide regions in a portion of a waveguide patternable film in accordance with another exemplary embodiment of the present invention is depicted.

[0037] Turning first to Fig. 5, a substrate 100 is shown having an essentially uniform thickness of a first layer 110 of a first varnish solution disposed thereon.

Generally, substrate 100 is a glass or quartz substrate, or a polyethylene terephthalate (PET) film.

[0038] In some embodiments of the present invention, the essentially uniform thickness of layer 110 is from about 5 μ m to about 200 μ m, while in other embodiments, layer 110 has a thickness of from about 10 μ m to about 100 μ m and in still other embodiments, layer 110 has a thickness of from about 15 μ m to about 65 μ m. While any of appropriate coating method, such as those discussed briefly above with respect to the embodiment of Figs. 1-3, may be used to dispose layer 110 on substrate 100, spreading the first varnish solution using a doctor blade has been found to be advantageous for forming such layer.

[0039] In Fig. 6, a waveguide patternable film 120 of a photo-induced thermally developable material (PITDM) is shown disposed over first varnish layer 110. It will be noted that layer 120 is advantageously formed over layer 110 by spreading a second varnish solution encompassing the PITDM using an appropriate spreading method without allowing layer 110 to substantially dry.

[0040] While it is believed to be desirable that the materials of layers 110 and 120 remain essentially distinct from one another, it is likely that as the second varnish solution is spread over a wet layer 110, some intermixing of the material of layer 110 and the material of the second varnish solution occurs. While not wishing to be bound to any theory, it is believed that such intermixing of the two materials can have a beneficial result in aiding to enhance the adhesion of layer 110 to layer 120 in a completed structure where such intermixing is controlled. One factor in having controlled intermixing, as well as to allow for the uniform spreading of the first and second varnish solutions to a desired thickness, is preparing such varnish solutions to have a desired viscosity. For example, it has been found advantageous in some embodiments of the present invention for the first and second varnish solutions to each have a viscosity from about 100 centipoise to about 10000 centipoise. Also advantageous is where the first and second varnish solutions each have a viscosity from about 150 centipoise to about 5000 centipoise and additionally where the first and second varnish solutions each have a viscosity from about 200 centipoise to about 3500 centipoise. In some embodiments in accordance with the present invention, it has been found that having the viscosity of the second varnish solution higher than the viscosity of the first varnish solution is advantageous. In some embodiments

of the present invention, layer 120 has an as spread thickness of from about 5 μ m to about 200 μ m, while in other embodiments layer 120 has a thickness of from about 15 μ m to about 125 μ m and in still other embodiments layer 120 has a thickness of from about 25 μ m to about 100 μ m.

[0041] Turning to Fig. 7, a layer 130 of a third varnish solution is shown disposed over waveguide patternable layer 120 to form a three-layer waveguide structure 200. Layer 130 is applied over layer 120 in a manner analogous to that described above for the application of layer 120 over layer 110. Also analogous is the belief that while it may be desirable for the materials of layers 120 and 130 to be essentially distinct from one another allowing some controlled intermixing may also be advantageous. Therefore, it has been found advantageous for the viscosity of the third varnish solution to have the same ranges of viscosity, provided above, as the first and/or second varnish solutions, and in some embodiments, for layers 110 and 130 to be formed using the same varnish solution.

[0042] With regard to thickness, in some embodiments of the present invention, layer 130 has an as spread thickness of from about 5 μ m to about 200 μ m, while in other embodiments layer 130 has a thickness of from about 10 μ m to about 100 μ m and in still other embodiments layer 130 has a thickness of from about 15 μ m to about 65 μ m. After second layer 130 is applied the three layer structure formed is heated to a temperature from about 25°C to about 40°C for about 15 minutes to about 60 minutes to allow for the evaporation of at least some of the solvent(s) used in the formulation of such varnish solutions.

[0043] It will be understood that in the three-layer structure 200 depicted in Fig. 7, waveguide structures, that is to say channel or core regions having laterally adjacent cladding regions, will be subsequently formed only in layer 120 in a manner analogous to forming of regions 40 and regions 25 in layer 10 (see, Fig. 3 and the description of the forming of such teachings/descriptions are applicable to the PITDM of layer 120 regions as provided above). It will further be understood that distinct from the embodiment of the present invention described in Figs. 1-3, as part of the forming process described with reference to embodiments of the present invention in accordance with Figs. 5-9 and the description herein, first and third varnish layers 110 and 130, respectively, will form cladding regions distinct from the laterally adjacent cladding regions

that will be formed within layer 120. Thus unlike waveguide structures previously known, for example the structures taught in the previously mentioned '620 patent, the additional steps of laminating cladding material or layers to the layer encompassing the waveguide cores is eliminated in the embodiments of the present invention described with reference to Figs. 5-9. It will also be understood, that while the spreading of the materials to form layers 120 and 130 has been described as spreading such materials over an underlying wet layer with no intervening period of time for such underlying layer to dry, in some embodiments of the present invention, some drying time is provided.

[0044] As previously mentioned, it is desirable for each of layers 110 and 130 to adhere to intervening layer 120 in the completed three-layer waveguide structure. It is believed that having some intermixing of the materials of layers 110 and 130 with the materials of layer 120 is beneficial in this regard. To aid in promoting the adhesion effect of such intermixing, or where essentially no physical intermixing occurs during the spreading of the several varnish solutions, some embodiments in accordance with the present invention encompass varnish solutions used for layers 110 and 130 that utilize analogous materials to those used for the varnish solution that forms layer 120. In this manner, it is believed that during the forming of the complete three-layer waveguide structure, polymerizations, such as those that occur within layer 120 to define core and clad regions, can also occur in any or all of (1) within layers 110 and 130, (2) within regions of intermixing at interfaces between adjacent layers, and (3) across such interfaces and/or interfacial regions.

[0045] Turning now to Fig. 8, portions of three-layer structure 200 are depicted being exposed to actinic radiation 300 through masking elements 350. As depicted, only regions 150 are exposed to actinic radiation 300 through masking elements 350; regions 140 are protected from such exposure by opaque portions of masking elements 350. The source of actinic radiation 300 is selected based on the sensitivity of the cationic photoinitiator selected to such radiation. Thus, where RHODORSIL® 2074 is employed in layer 120, a mercury vapor lamp is used as an ultraviolet (UV) radiation source to provide sufficient energy below 300 nanometers (nm) to cause the decomposition of the Rhodorsil and provide the cation and WCA as mentioned above within exposed regions 150.

[0046] It will also be understood that while masking element 350 is depicted as only having two openings for allowing radiation 300 to pass through to regions 150, such a depiction is simplified, and masking element 350 can be provided having a variety of more complex patterns to define one or more optical waveguide elements and/or coupling devices.

[0047] Referring now to Fig. 9, the structure of Fig. 8 is depicted after thermal curing. That is to say, the structure of Fig. 9 was heated to a first temperature for a first period of time to allow for the removal of any residual solvents with structure 200, then to a second temperature, higher than the first, for a second period of time and finally to a third temperature, higher than the second, for a third period of time. The second temperature is sufficient to cause active but latent catalyst to become an active catalyst and cause the polymerization of the norbornene-type monomers within exposed regions 150. Advantageously, it has been found that in addition to the polymerization of the norbornene-type monomers originally dispersed within regions 150 at the time of the exposure to actinic radiation 300, additional norbornene-type monomers diffuse into exposed regions 150 from unexposed regions 140 of film 120 and are polymerized therein. It will be understood that the exposure and thermal curing of layers of structure 200 are analogous to such exposure and curing described for the embodiment of Figs. 1-3. Thus after the second period of time a waveguide pattern is generally visible within structure 200 where one of exposed and unexposed regions 150 and 140, respectively, is a core region and the other is a laterally adjacent cladding region.

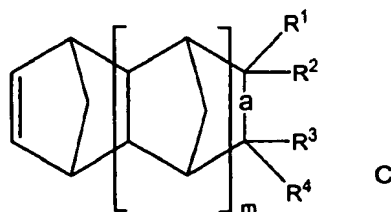
[0048] While the second temperature and period of time are generally sufficient for polymerization within regions 150 to be substantially complete, it is advantageous for the third temperature to be sufficiently high to cause any remaining cationic photoinitiator to thermally decompose and form the same species as previously described being caused by radiation 300. It is believed, again without wishing to be bound by theory of invention, that the third heating results not only in the polymerization of any residual, not yet polymerized, norbornene-type monomers within exposed regions 150, but also causes the polymerization of any of such monomers remaining in unexposed regions 140. In this manner, heating to the third temperature serves to stabilize the resulting structure of optical waveguide channel (or core) having laterally adjacent cladding regions.

[0049] It should be realized that while structure 200 and the processing thereof is analogous to the embodiment of Figs. 1-3, structure 200 encompasses additional

layers 110 and 130 which underlie and overlie, respectively, layer 120. Generally, like layer 120, layers 110 and 130 also include a photoinitiator, a procatalyst, a polymer matrix and monomers. However, as such layers are intended to serve as cladding layers, the polymer matrix of layers 110 and 130 is selected to be different from the polymer matrix employed for layer 120. For example, where the polymer matrix of layer 120 has a relatively high refractive index (RI), the polymer matrix of layers 110 and 130 would have a relatively low RI. In this manner, the forming of distinct core and clad regions in layers 110 and 130 is avoided. In addition, the monomer selected for such layers is generally the same monomer utilized in layer 120 and as the catalyst to monomer ratio is generally adjusted lower than that of layer 120, it is believed that monomer from layers 110 and 130 diffuse into layer 120 and are included into polymer chains that are included within at least two adjacent layers and predominately formed during the heating to the second temperature for the second period of time. In this manner it is believed that adhesion between such adjacent layers is enhanced. It should be noted that other formulations of the varnish solutions used for layers 110 and 130 are contemplated and/or have been evaluated. For example, in some embodiments of the present invention varnish solutions for layers 110 and 130 incorporate norbornene-type polymers where at least one of the norbornene-type repeat units encompasses a pendant group having an epoxide moiety, and an acid generating material to provide for opening the aforementioned epoxide moiety.

Monomers

[0050] The norbornene-type monomers in accordance with the present invention are represented by Structure C below:



wherein "a" represents a single or double bond, R^1 to R^4 independently represent a hydrogen, hydrocarbyl or functional substituent, m is an integer from 0 to 5, and when "a" is a double bond when one of R^1 , R^2 and one of R^3 , R^4 are not present.

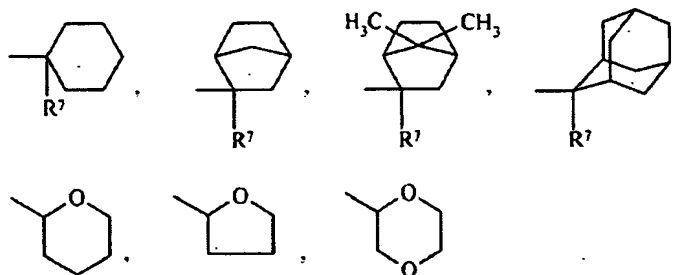
[0051] When the substituent is a hydrocarbyl group, R^1 to R^4 can be a halohydrocarbyl, or perhalohydrocarbyl group, or even a perhalocarbyl group (e.g., a trifluoromethyl group). In one embodiment, R^1 to R^4 independently represent hydrocarbyl, halogenated hydrocarbyl and perhalogenated hydrocarbyl groups selected from hydrogen, linear or branched C_1 - C_{10} alkyl, linear or branched, C_2 - C_{10} alkenyl, linear or branched C_2 - C_{10} alkynyl, C_4 - C_{12} cycloalkyl, C_4 - C_{12} cycloalkenyl, C_6 - C_{12} aryl, and C_7 - C_{24} aralkyl, R^1 and R^2 or R^3 and R^4 can be taken together to represent a C_1 - C_{10} alkylidenyl group. Representative alkyl groups include but are not limited to methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert butyl, pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, and decyl. Representative alkenyl groups include but are not limited to vinyl, allyl, butenyl, and cyclohexenyl. Representative alkynyl groups include but are not limited to ethynyl, 1 propynyl, 2-propynyl, 1 butynyl, and 2-butylnyl. Representative cycloalkyl groups include but are not limited to cyclopentyl, cyclohexyl, and cyclooctyl substituents. Representative aryl groups include but are not limited to phenyl, naphthyl, and anthracenyl. Representative aralkyl groups include but are not limited to benzyl, and phenethyl. Representative alkylidenyl groups include methylidenyl, and ethylidenyl, groups.

[0052] In one embodiment, the perhalohydrocarbyl groups include perhalogenated phenyl and alkyl groups. The halogenated alkyl groups useful in the invention are partially or fully halogenated and are linear or branched, and have the formula C_zX^{z+1} wherein X is independently a halogen or a hydrogen and z is selected from an integer of 1 to 20. In another embodiment, each X is independently selected from hydrogen, chlorine, fluorine and/or bromine. In yet another embodiment, each X is independently either a hydrogen or a fluorine.

[0053] In another embodiment, the perfluorinated substituents include perfluorophenyl, perfluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, and perfluorohexyl. In addition to the halogen substituents, the cycloalkyl, aryl, and aralkyl groups of the invention can be further substituted with linear or branched C_1 - C_5 alkyl and haloalkyl groups, aryl groups and cycloalkyl groups.

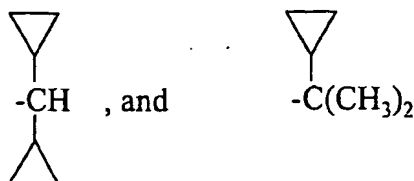
[0054] When the pendant group(s) is(are) a functional substituent, R^1 to R^4 independently represent a radical selected from $(CH_2)_n-CH(CF_3)_2-O-Si(Me)_3$, $-(CH_2)_n-CH(CF_3)_2-O-CH_2-O-CH_3$, $-(CH_2)_n-CH(CF_3)_2-O-C(O)-O-C(CH_3)_3$, $-(CH_2)_n-C(CF_3)_2-OH$, $(CH_2)_n-C(O)NH_2$, $(CH_2)_n-C(O)Cl$, $(CH_2)_n-C(O)OR^5$, $(CH_2)_n-OR^5$, $-(CH_2)_n-OC(O)R^5$, $(CH_2)_n-C(O)R^5$, $(CH_2)_n-OC(O)OR^5$, $(CH_2)_nSi(R^5)_3$, $-(CH_2)_nSi(OR^5)_3$, $-(CH_2)_n-O-Si(R^5)_3$, and $(CH_2)_n-C(O)OR^6$ wherein n independently

represents an integer from 0 to 10 and R^5 independently represents hydrogen, linear or branched C_1 - C_{20} alkyl, linear or branched C_1 - C_{20} halogenated or perhalogenated alkyl, linear or branched C_2 - C_{10} alkenyl, linear or branched C_2 - C_{10} alkynyl, C_5 - C_{12} cycloalkyl, C_6 - C_{14} aryl, C_6 - C_{14} halogenated or perhalogenated aryl, and C_7 - C_{24} aralkyl. Representative hydrocarbyl groups set forth under the definition of R^5 are the same as those identified above under the definition of R^1 to R^4 . As set forth above under R^1 to R^4 the hydrocarbyl groups defined under R^5 can be halogenated and perhalogenated. For example, when R^5 is C_1 - C_{20} halogenated or perhalogenated alkyl, R^5 can be represented by the formula $C_zX^{n_{2z+1}}$, wherein z and X^n are defined as above, and at least one X^n on the alkyl group must be a halogen (e.g., Br, Cl, or F). It is to be recognized that when the alkyl group is perhalogenated, all X^n substituents are halogenated. Examples of perhalogenated alkyl groups include, but are not limited to, trifluoromethyl, trichloromethyl, $-C_7F_{15}$, and $-C_{11}F_{23}$. Examples of perhalogenated aryl groups include, but are not limited to, pentachlorophenyl and pentafluorophenyl. The R^6 radical represents an acid labile moiety selected from $-C(CH_3)_3$, $-Si(CH_3)_3$, $CH(R^7)OCH_2CH_3$, $-CH(R^7)OC(CH_3)_3$ or the following cyclic groups:



wherein R^7 represents hydrogen or a linear or branched (C_1 - C_5) alkyl group. The alkyl groups include methyl, ethyl, propyl, i-propyl, butyl, i butyl, t butyl, pentyl, t-pentyl and neopentyl. In the above structures, the single bond line projecting from the cyclic groups indicates the position where the cyclic protecting group is bonded to the acid substituent. Examples of R^6 radicals include 1-methyl-1-cyclohexyl, isobornyl, 2-methyl-2-isobornyl, 2 methyl-2-adamantyl, tetrahydrofuranlyl, tetrahydropyranoyl, 3 oxocyclohexanonyl, mevalonic lactonyl, 1 ethoxyethyl, and 1-t-butoxy ethyl.

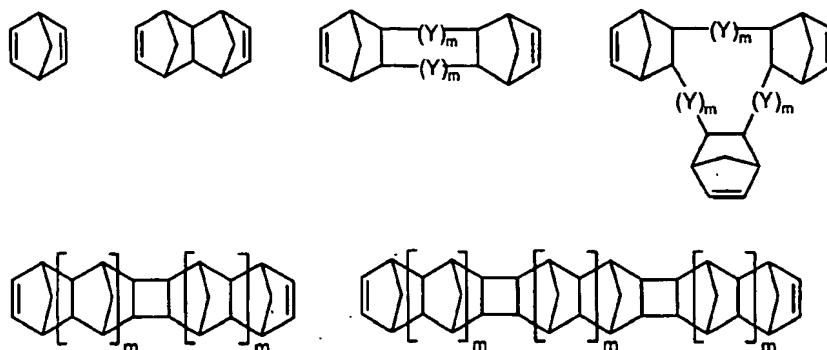
[0055] The R^6 radical can also represent dicyclopropylmethyl (Dcpm), and dimethylcyclopropylmethyl (Dmcp) groups which are represented by the following structures:



[0056] The polymer matrix used in forming films encompassing a photo-induced thermally developable material (PITDM), in accordance with the present invention, is polymerized using monomers such as discussed above. Where it is desired that such matrix have a relatively high RI, monomers are selected that will result, after polymerization, in the polymer matrix having the desired relatively high RI. As a general rule, such monomers are those molecules that contain aromatic, nitrogen, Br or Cl moieties. Alternatively, where it is desired that the polymer matrix have a relatively low RI, monomers are selected that will result in the polymer matrix having the desired relatively low RI. As a general rule, such low RI monomers are those molecules that contain alkyl, F and/or ether moieties. In addition, norbornene-type monomers used in forming any of the varnish solutions discussed herein, use monomers such as discussed above. It will be noted that where such monomers are included in a varnish solution to polymerize in predetermined regions after exposure of such portion to actinic radiation and thus alter the RI of predetermined regions, such monomers are appropriately selected.

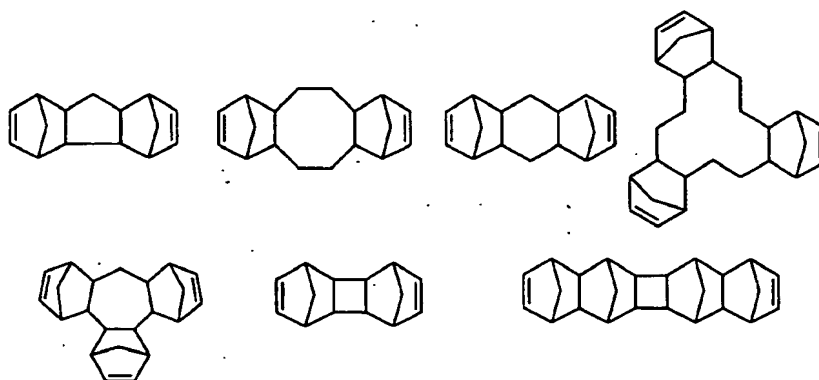
Crosslinking Monomers

[0057] Crosslinked polymers can be prepared by copolymerizing the norbornene-type monomer(s) set forth under Structure C above with a multifunctional norbornene-type crosslinking monomer. By multifunctional norbornene-type crosslinking monomer is meant that the crosslinking monomer contains at least two norbornene-type moieties (norbornene-type double bonds), each functionality being polymerizable in the presence of the catalyst system of the present invention. The crosslinkable monomers include fused multicyclic ring systems and linked multicyclic ring systems. Examples of fused crosslinking agents are illustrated in structures below. For brevity, norbornadiene is included as a fused multicyclic crosslinking agent and is considered to contain two polymerizable norbornene-type double bonds.

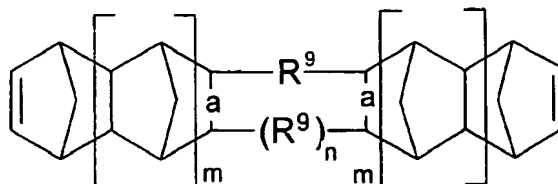


wherein Y represents a methylene ($-\text{CH}_2-$) group and m independently represents an integer from 0 to 5, and when m is 0, Y represents a single bond.

Representative monomers under the forgoing formulae are set forth below.



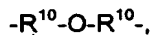
[0058] A linked multicyclic crosslinking agent is illustrated generically by the following structure:



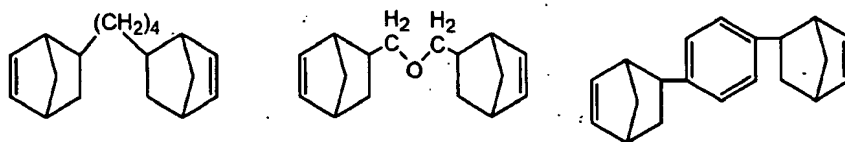
wherein "a" independently represents a single or double bond, m independently is an integer from 0 to 5, R^9 is a divalent radical selected from divalent hydrocarbyl radicals, divalent ether radicals and divalent silyl radicals, and n is equal to 0 or 1. By divalent is meant that a free valence at each terminal end of the radical is attached to a norbornene-type moiety. In one embodiment, the divalent

hydrocarbyl radicals are alkylene radicals and divalent aromatic radicals. The alkylene radicals are represented by the formula $-(C_dH_{2d})-$ where d represents the number of carbon atoms in the alkylene chain and is an integer from 1 to 10. The alkylene radicals are, in one embodiment, selected from linear or branched (C_1 to C_{10}) alkylene such as methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, and decylene. When branched alkylene radicals are contemplated, it is to be understood that a hydrogen atom in the alkylene backbone is replaced with a linear or branched (C_1 to C_5) alkyl group.

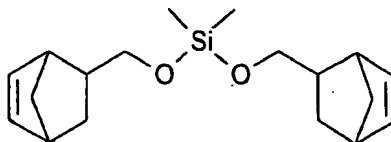
[0059] The divalent aromatic radicals are selected from divalent phenyl, and divalent naphthyl radicals. The divalent ether radicals are represented by the group



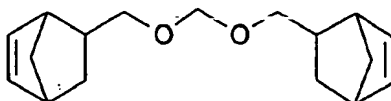
wherein R^{10} independently is the same as R^9 . Examples of specific linked multicyclic crosslinking agents are represented as the following structures:

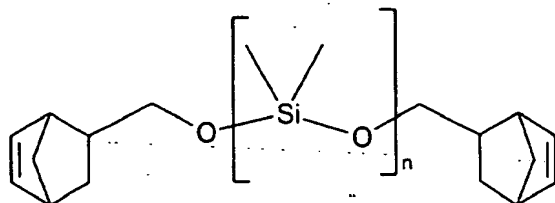


[0060] In one embodiment, the crosslinking agent is selected from those shown below:

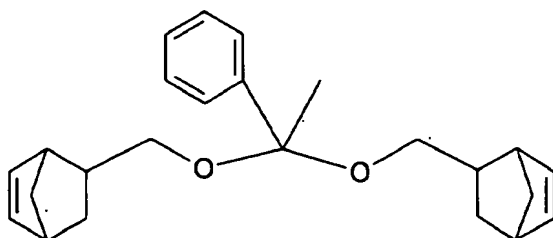
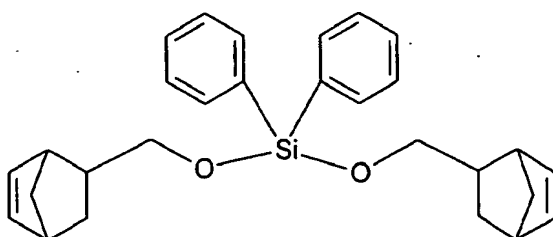
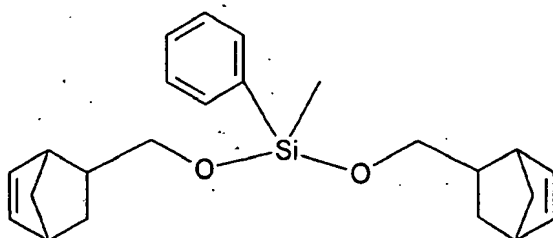
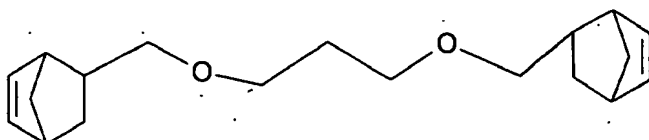
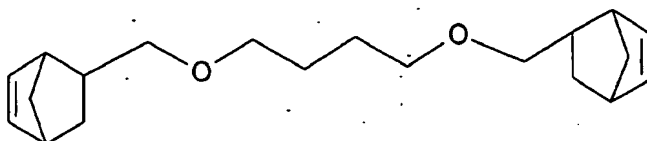


which is dimethyl bis[bicyclo[2.2.1]hept-2-ene-5-methoxy] silane (also referred to herein as dimethyl bis(norbornene methoxy) silane),

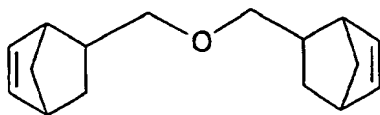




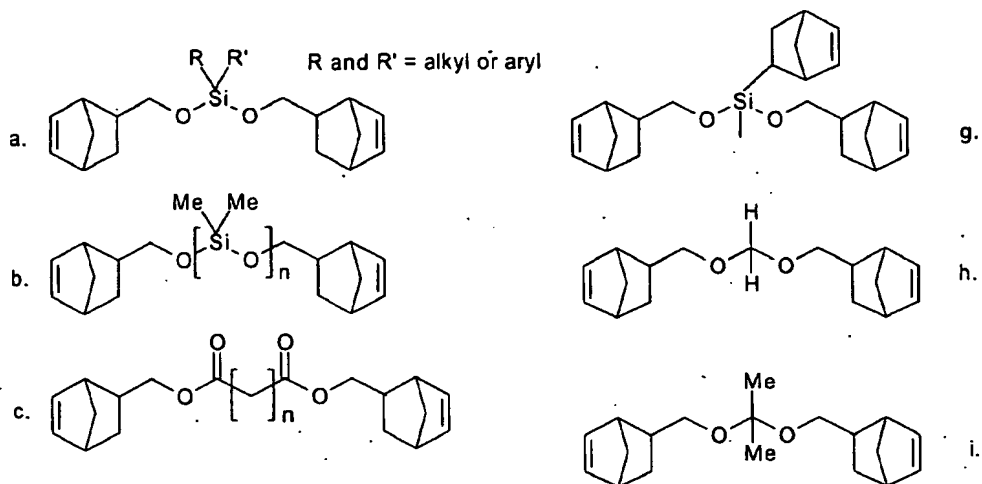
where n is 1 to 4,

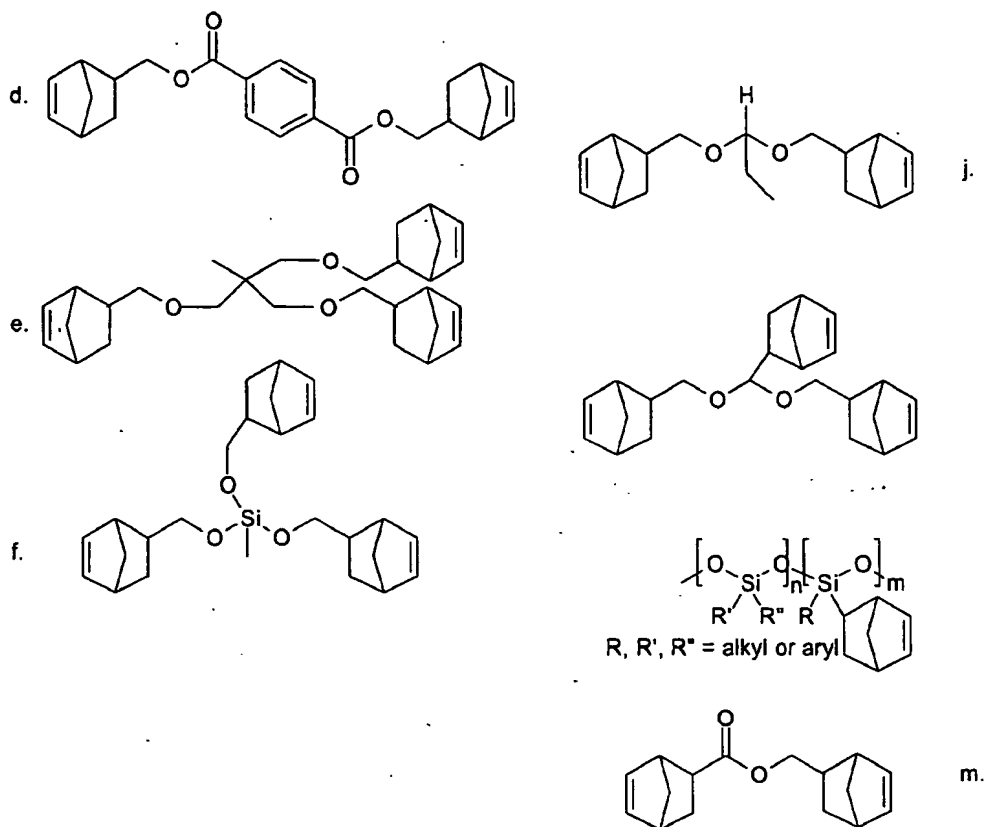


, and

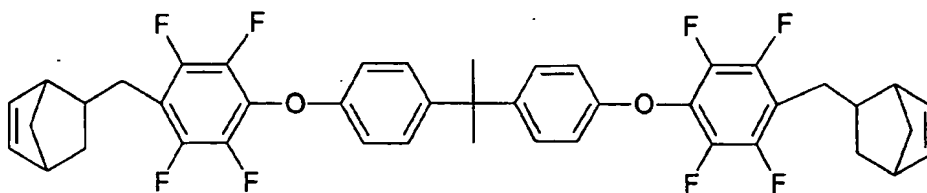


[0061] Some other types of norbornene-based crosslinking agents include, but are not limited to, those represented in formulae a-m below.



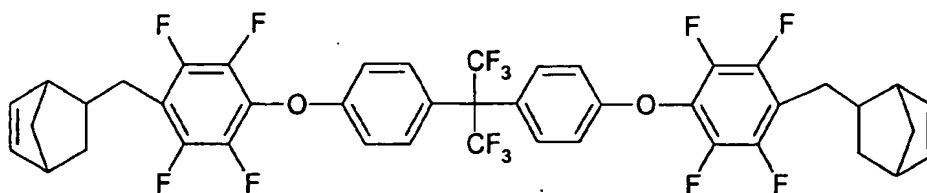


[0062] In another embodiment, fluorine-containing norbornene-based cross linkers are used. For example, in one embodiment one or more of the following fluorinated norbornene crosslinking agents can be utilized.



F - Crosslinking Agent I

and



F - Crosslinking Agent II.

[0063] After forming the polymer matrix having the desired RI, a solution of such matrix polymer and other materials is formed. As mentioned above, the other materials include, but are not limited to, one or more distinct norbornene-type monomers where at least one of such monomers is a crosslinking norbornene-type monomer, such as described above, a cationic photoinitiator and, where desired, an antioxidant. It will be understood the RI of such solution is altered, that is to say either higher or lower than, the RI of the polymer matrix. The specific norbornene-type monomers selected to form this solution are a function of what relative RI is desired for regions of the, to be formed, film that will be exposed as well as the RI of the matrix polymer. Thus where an exposed region having a relatively high RI is desired, embodiments in accordance with the present invention can combine a polymer matrix with a relatively low RI with norbornene-type monomers that when polymerized will result in a relatively high RI in such exposed region. However, it will be understood that alternate combinations of polymer matrix and norbornene-type monomers can be used to generate exposed and unexposed regions having different refractive indices such that one or more waveguide cores or channels and laterally adjacent cladding regions are formed.

[0064] It will be understood that the terms high or relatively high RI and low or relatively low RI do not refer to absolute values of RI. Rather such terms are merely indicative of the relationship of the RI of regions, polymers or materials to one another. In other words, a material or polymer having a high RI is only considered as being high when compared to another material, polymer or region having a lower RI. Thus no reference to high or low values of RI, herein, should be interpreted as meaning anything other than a value relative to another RI.

Procatalysts

[0065] As mentioned above, some embodiments in accordance with the present invention encompass procatalyst moieties represented by formula I:



where R, E and Q are as previously defined. Exemplary procatalysts in accordance with formula I include, but are not limited to $Pd(P\text{-}i\text{-}Pr_3)_2(OAc)_2$, $Pd(PCy_3)_2(OAc)_2$, $Pd(PCy_3)_2(O_2CCMe_3)_2$, $Pd(PCp_3)_2(OAc)_2$, $Pd(PCy_3)_2(O_2CCF_3)_2$ and $Pd(PCy_3)_2(O_2CC_6H_5)_3$.

[0066] The following procatalyst synthesis examples C1-C4 demonstrate the preparation of several exemplary procatalysts useful in embodiments of the present invention.

Example C1

Preparation of $\text{Pd}(\text{OAc})_2(\text{P}(i\text{-Pr})_3)_2$

[0067] In a N_2 filled flask equipped with an addition funnel, a CH_2Cl_2 solution (20 mL) of $\text{P}(i\text{-Pr})_3$ (8.51 mL, 44.6 mmol) was added drop-wise to a -78°C stirring reddish brown suspension of $\text{Pd}(\text{OAc})_2$ (5.00 g, 22.3 mmol) in CH_2Cl_2 (30 mL). The suspension gradually cleared to a yellow green solution which was allowed to warm to room temperature, stirred for two hours and then filtered through a $0.45\ \mu\text{m}$ filter. Concentration of the filtrate to approximately 10 mL followed by addition of hexanes (20 mL) afforded yellow solids which were filtered off (in air), washed with hexanes ($5 \times 5\ \text{mL}$) and dried in vacuo. Yield 10.937 g (89 %). NMR data: ^1H NMR (δ , CD_2Cl_2): 1.37 (dd, 36H, CHCH_3), 1.77 (s, 6H, CCH_3), 2.12 (m, 6H, CH). ^{31}P NMR (δ , CD_2Cl_2): 32.9 (s).

Example C2

Preparation of $\text{Pd}(\text{OAc})_2(\text{P}(\text{Cy})_3)_2$

[0068] In a two-neck round bottom flask equipped with an addition funnel, a reddish brown suspension of $\text{Pd}(\text{OAc})_2$ (5.00 g, 22.3 mmol) in CH_2Cl_2 (50 mL) was set to stir at -78°C . The addition funnel was charged with a CH_2Cl_2 solution (30 mL) of $\text{P}(\text{Cy})_3$ (13.12 g, 44.6 mmol) which was then added drop-wise to the stirring suspension over the course of 15 minutes resulting in a gradual change from reddish brown to yellow. After 1 hour of stirring at -78°C the suspension was allowed to warm to room temperature, stirred for an additional two hours and then diluted with hexanes (20 mL). The yellow solids were then filtered off in air, washed with pentane ($5 \times 10\ \text{mL}$) and dried in vacuo. A second crop was isolated by cooling the filtrate to 0°C and filtering, washing and drying as previously described. Yield 15.42 g (88 %). NMR data: ^1H NMR (δ , CD_2Cl_2): 1.18 - 1.32 (br m, 18H, Cy), 1.69 (br m, 18H, Cy), 1.80 (br m, 18H, Cy) 1.84 (s, 6H, CH_3), 2.00 (br d, 12 H, Cy). ^{31}P NMR (δ , CD_2Cl_2): 21.2 (s).

Example C3

Preparation of $\text{trans-Pd}(\text{O}_2\text{C-}t\text{-Bu})_2(\text{P}(\text{Cy})_3)_2$

[0069] $\text{Pd}(\text{O}_2\text{C-}t\text{-Bu})_2$ (1.3088 g, 4.2404 mmol) was dispersed in CH_2Cl_2 (10 mL) in a 100 mL Schlenk flask, the contents of the flask was cooled to -78°C and stirred. To the above solution was slowly added the CH_2Cl_2 (15 mL) solution of

P(Cy)₃ (2.6749 g, 9.5382 mmol) via a syringe, stirred for an hour at -78 °C and at room temperature for 2 hours. Hexane (20 mL) was added to the above reaction mixture to give the title complex as a yellow solid (1.391 g). The solid was filtered, washed with hexane (10 mL) and dried under reduced pressure. Solvent was removed from the filtrate to give an orange solid which was then dissolved in CHCl₃/hexane mixture (1/1: v/v) and the resulting solution was evaporated inside a fume hood to give more of the title complex (648 mg). Total yield = 2.039g (2.345 mmol), 55.3%. Analysis Calc'd for C₄₆H₈₄O₄P₂Pd: C 63.54, H 9.74%.

Example C4

Preparation of Pd(OAc)₂(P(Cp)₃)₂

[0070] In a N₂ filled flask, a reddish brown suspension of Pd(OAc)₂ (2.00g, 8.91mmol) in CH₂Cl₂ (~25 mL) was set to stir at -78°C. With a cannula, P(Cp)₃ (4.25, 17.83 mmol) in CH₂Cl₂ (~20 mL) was added drop wise to the stirring suspension over the course of 10 minutes resulting in a gradual change from orange brown to yellow. The suspension was allowed to warm to room temperature and stirred for an additional 1 hour. Concentration of the solvent (~ 5 mL) followed by addition of hexanes (~15 mL) afforded yellow solids which were filtered off in air, washed with hexanes (5 x 10 mL) and dried in vacuo. A second crop was isolated by cooling the filtrate to 0°C and filtering, washing, and drying as set forth in Example 3. Yield 4.88 g (85%). NMR data: ¹H NMR (δ, CD₂Cl₂): 1.52 - 1.56 (br m, 12H, Cp₃), 1.67 - 1.72 (br m, 12H, Cp₃), 1.74 (s, 6H, CH₃), 1.85 - 1.89 (br m, 12H, Cp₃), 1.96 - 1.99 (br d, 6H, Cp₃), 2.03 - 2.09 (br m, 12H, Cp₃). ³¹P NMR (δ, CD₂Cl₂): 22.4 (s).

Examples P1-P10

[0071] Examples P1 – P10 demonstrate the synthesis of norbornene-type polymers useful as matrix polymers for photo-induced thermally developable materials used in accordance with embodiments of the present invention.

Example P1

Synthesis of Hexyl Norbornene/ Diphenylmethyl Norbornenemethoxy Silane Copolymer (P1)

[0072] HxNB (8.94g, 0.05mol), diPhNB (16.1g, 0.05mol), 1-hexene (4.2 g, 0.05mol) and toluene (142.0g) were combined in a 250mL serum bottle and heated to 120°C in an oil bath to form a solution. To this solution were added [Pd(PCy₃)₂(O₂CCH₃)(NCCH₃)]tetrakis(pentafluorophenyl)borate (Pd1446) (5.8E-3 g, 4.0E-6 mol) and N, N-dimethylanilinium tetrakis(pentafluorophenyl)borate

(DANFABA) ($3.2\text{E-}3$ g, $4.0\text{E-}6$ mol), each in the form of a concentrated dichloromethane solution. After addition, the resulting mixture was maintained at 120°C for 6 hours. The copolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 80°C under vacuum. After drying, 12.0g was obtained (48%). The molecular weight of the copolymer was determined by GPC in THF solvent (polystyrene standard) to be $M_w = 16,196$ and $M_n = 8,448$. The composition of the copolymer was determined by $^1\text{H-NMR}$ to be 54/46 HxNB/diPhNB. The dried copolymer was dissolved in sufficient mesitylene to result in a 10 wt% copolymer solution.

Example P2

Synthesis of Hexyl Norbornene / Phenethyl Norbornene Copolymer (P2)

[0073] HxNB (2.78g, 0.0156mol), Phenyl ethyl norbornene (PENB, CAS 29415-09-6) (7.22g, 0.036mol), 1-hexene (2.18g, 0.026mol) and toluene (57.0g) were combined in a 250mL serum bottle and heated to 120°C in an oil bath. To this solution were added Pd1446 ($3.0\text{E-}3$ g, $2.1\text{E-}6$ mol) and DANFABA ($6.7\text{E-}3$ g, $8.4\text{E-}6$ mol) in concentrated solutions of dichloromethane. After addition, the resulting mixture was maintained at 120°C for 1 hour. After cooling to room temperature, the copolymer was precipitated by adding methanol drop wise into the reaction mixture. The solid copolymer was collected by filtration and dried at 80°C in a vacuum oven. The solid polymer was dissolved in an appropriate amount of mesitylene to give 10wt% solid copolymer solution. After drying, 8.0g was obtained (80%). The molecular weight of the polymer was determined by GPC methods in THF (poly(styrene) standard) $M_w = 127,332$; $M_n = 39,206$. The composition of the polymer was determined by $^1\text{H-NMR}$: HxNB/PENB = 22/78.

Example P3

Synthesis of HxNB/diPhNB Copolymer (P3)

[0074] HxNB (8.94g, 0.050mol), diPhNB (16.1g, 0.050mol), 1-hexene (2.95g, 0.035mol) and toluene (142g) were weighed out in a 250mL serum bottle and heated at 80°C in an oil bath. To this solution were added ($5.8\text{E-}3$ g, $4.0\text{E-}6$ mol) of Pd1446 and ($3.2\text{E-}3$ g, $4.0\text{E-}6$ mol) of DANFABA. The ratio of norbornene monomers/Pd1446/DANFABA was 25K/1/1. The mixture was maintained at 80°C for 7h after which the activity of the Pd catalyst was quenched by adding 20mL of acetonitrile. Thereafter, the polymer was precipitated by adding methanol drop-wise to the reaction mixture. The precipitated copolymer was collected by

filtration and dried at 65°C in a vacuum oven. Then the copolymer was dissolved in mesitylene to give 10wt% solid copolymer solution. After drying, 19.8g was obtained (79%). The polymer's molecular weight was determined by GPC methods in THF using poly(styrene) as a standard: $M_w = 86,186$; $M_n = 21,602$. The ratio of HxNB/diPhNB in the polymer was determined by $^1\text{H-NMR}$: HxNB/diPhNB = 46/54. The refractive indices of this polymer were measured by prism coupling method and determined to be 1.5569 in TE mode and 1.5556 in TM mode at a wavelength of 633nm.

Example P4

Synthesis of HxNB/diPhNB Copolymer (P4)

[0075] HxNB (8.94g, 0.050mol), diPhNB (16.1g, 0.050mol), 1-hexene (20.0g, 0.239mol) and toluene (142g) were weighed out into a 250mL serum bottle and heated at 80°C in an oil bath to form a solution. To this solution were added Pd1446 (5.80E-3g, 4.0E-6 mol) and DANFABA (3.21E-3g, 4.01E-6 mol). The mixture was maintained at 80°C for 6h after which the activity of the Pd catalyst was quenched by adding 20mL of acetonitrile. Thereafter, the polymer was precipitated by adding methanol drop-wise to the reaction mixture. The precipitated copolymer was collected by filtration and dried at 65°C in a vacuum oven. Then the polymer was dissolved in mesitylene to give 10wt% solid copolymer solution. The polymer's molecular weight was determined by GPC methods in THF using poly(styrene) as a standard: $M_w = 20,586$; $M_n = 11,613$. The ratio of HxNB/diPhNB in the polymer was determined by $^1\text{H-NMR}$: HxNB/diPhNB = 60/40.

Example P5

Synthesis of Hexylbornene / Diphenylmethyl Norbornenemethoxy Silane Copolymer (P5)

[0076] HxNB, (8.94g, 0.050mol), diPhNB, (16.06g, 0.050mol), 1-hexene (5.0 g, 0.060mol) and toluene (142g) were combined in a 500mL serum bottle and heated to 80°C in an oil bath to form a solution. To this solution were added Pd1446, (2.90E-3 g, 2.00E-6 mol), and DANFABA, (3.2E-3 g, 4.01E-6 mol) each in the form of a concentrated solution of dichloromethane. After the addition, the resulting mixture was maintained at 80°C for 6 hours. The copolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 60°C under vacuum. After drying, 19.3g was obtained (77%). The molecular weight of the copolymer, determined by GPC in THF solvent (polystyrene standard) provided $M_w = 58,749$ and $M_n = 18,177$. The composition of the copolymer was determined

by $^1\text{H-NMR}$ to be 53/47 HxNB/diPhNB. The refractive indices of this polymer were measured by prism coupling method and determined to be 1.5572 in TE mode and 1.5558 in TM mode at a wavelength of 633nm.

Example P6

Synthesis of Butylnorbornene / Diphenylmethyl Norbornenemethoxy Silane Copolymer (P6)

[0077] Butyl Norbornene (BuNB, CAS 22094-81-1) (2.62g, 0.038mol), diPhNB, (22.38g, 0.057mol), 1-hexene (8.83g, 0.011mol) and toluene (141.4g) were combined in a 500mL serum bottle and heated to 80°C in an oil bath to form a solution. To this solution were injected Pd1446, (5.05E-3 g, 3.49E-6 mol) and DANFABA (1.12E-2 g, 1.40E-5 mol) each in the form of a concentrated solution in dichloromethane. After addition, the resulting mixture was maintained at 80°C for 2 hours. The copolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 60°C under vacuum. After drying, 7.5g was obtained (30%). The molecular weight of the copolymer, determined by GPC in THF solvent (polystyrene standard) provided $M_w = 32,665$ and $M_n = 19,705$. The composition of the copolymer was determined by $^1\text{H-NMR}$ to be 28/72 HxNB/diPhNB. The refractive indices of this polymer were measured by prism coupling method and determined to be 1.5785 in TE mode and 1.5771 in TM mode at a wavelength of 633nm.

Example P7

Synthesis of Hexylnorbornene / Diphenylmethyl Norbornenemethoxy Silane copolymer (P7)

[0078] HxNB, (8.987g, 0.050mol), diPhNB, (16.08g, 0.050mol), 1-hexene (2.976 g, 0.0354mol) and toluene (141.5g) were combined in a 500mL serum bottle and heated to 80°C in an oil bath to form a solution. To this solution were added Pd1446, (5.80E-3 g, 4.01E-6 mol) and DANFABA (3.2E-3 g, 4.0E-6 mol) each in the form of a concentrated solution in dichloromethane. After addition, the resulting mixture was maintained at 80°C for 6 hours. The copolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 60°C under vacuum. After drying, 19.8g was obtained (79%). The molecular weight of the copolymer, determined by GPC in THF solvent (polystyrene standard) provided $M_w = 86,186$ and $M_n = 21,602$. The composition of the copolymer was determined by $^1\text{H-NMR}$ to be 46/54 HxNB/diPhNB. The refractive indices of this polymer were

measured by prism coupling method and determined to be 1.5569 in TE mode and 1.5556 in TM mode at a wavelength of 633nm

Example P8

Synthesis of Hexyl Norbornene Homopolymer (P8)

[0079] HxNB, (10.0g, 0.056mol), 1-hexene (4.71g, 0.056mol) and toluene (56.7g) were combined in a 250mL serum bottle and heated to 80°C in an oil bath to form a solution. To this solution were added Pd1446, (4.10E-4 g, 2.80E-7 mol) and DANFABA, (2.20E-4 g, 2.80E-7 mol), each in the form of a concentrated solution in dichloromethane. After addition, the resulting mixture was maintained at 80°C for 40 minutes. The homopolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 60°C under vacuum. After drying, 5.8g was obtained (58%). The molecular weight of the copolymer, determined by GPC in THF solvent (polystyrene standard) provided $M_w = 121,541$ and $M_n = 59,213$. The refractive indices of this polymer were measured by prism coupling method and determined to be 1.5146 in TE mode and 1.5129 in TM mode at a wavelength of 633nm.

Example P9

Synthesis of HexylNorbornene / Diphenylmethyl Norbornenemethoxy Silane Copolymer (P9)

[0080] HxNB, (9.63g, 0.054mol), diPhNB, CAS 376634-34-3) (40.37g, 0.126mol), 1-hexene (4.54g, 0.054mol) and toluene (333g) were combined in a 500mL serum bottle and heated to 80°C in an oil bath to form a solution. To this solution were added Pd1446, (1.04E-2 g, 7.20E-6 mol) and N, N-dimethylanilinium tetrakis(pentafluorophenyl)borate (DANFABA) (2.30E-2 g, 2.88E-5 mol) each in the form of a concentrated solution of dichloromethane. After addition, the resulting mixture was maintained at 80°C for 2 hours. The copolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 60°C under vacuum. After drying, 19.0g was obtained (38%). The molecular weight of the copolymer, determined by GPC in THF solvent (polystyrene standard) provided $M_w = 118,000$ and $M_n = 60,000$. The composition of the copolymer was determined by $^1\text{H-NMR}$ to be 32/68 HxNB/diPhNB. The refractive indices of this polymer were measured by prism coupling method and determined to be 1.5695 in TE mode and 1.5681 in TM mode at a wavelength of 633nm

Example P10

Synthesis of HexylNorbornene / Diphenylmethyl Norbornenemethoxy Silane copolymer (P10)

[0081] HxNB (9.63g, 0.054mol), diPhNB (1.92g, 0.006 mol), 1-hexene (5.04g, 0.060mol) and toluene (56.7g) were combined in a 250mL serum bottle and heated to 80°C in an oil bath to form a solution. To this solution were injected Pd1446 (4.30E-4 g, 3.00E-7 mol) and DANFABA (2.40E-4 g, 3.00E-7 mol), each in the form of a concentrated solution in dichloromethane. After addition, the resulting mixture was maintained at 80°C for 2 hours. The copolymer was precipitated by adding methanol drop wise into the vigorously stirred reaction mixture. The precipitated copolymer was collected by filtration and dried in an oven at 60°C under vacuum. After drying, 7.7g was obtained (67%). The molecular weight of the copolymer was determined by GPC in THF solvent (polystyrene standard) to be $M_w = 82,000$ and $M_n = 40,000$. The refractive indices of this polymer were measured by prism coupling method and determined to be 1.5238 in TE mode and 1.5225 in TM mode at a wavelength of 633nm.

Examples V1-V13

[0082] Examples V1–V13 demonstrate the formulation of varnish solutions encompassing matrix polymers, norbornene-type monomers, a procatalyst, an acid generator, optional antioxidants and solvents in accordance with embodiments of the present invention. It will be noted that as each of the varnish solutions exemplified below incorporates a photo sensitive material, such solutions were formulated under yellow light.

Example V1

[0083] HxNB (42.03g, 0.24 mol) and bis-Norbornenemethoxy dimethylsilane (SiX, CAS 376609-87-9) (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX® 1076 (0.5g) and Ciba® IRGAFOS® 168 (0.125g) (both available from Ciba Specialty Chemicals Corporation, Tarrytown, NY) to form a monomer-antioxidant solution. To 30.0g of the above prepared P1 copolymer solution, were added 3.0g of the monomer-antioxidant solution, Pd(PCy₃)₂(OAc)₂ (Pd785) (4.94E-4g, 6.29E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (CAS 178233-72-2, available from Rhodia Inc, Cranbury, N.J.) (2.55E-3g, 2.51E-6 mol in 0.1 mL of methylene chloride) to form the varnish solution. The varnish solution was filtered through a 0.2-micron pore filter prior to use.

Example V2

[0084] SiX (5g, 0.0164mol) was weighed out in a glass vial. To the SiX were added Irganox 1076 (0.05g) and Irgafos 168 (0.013g) to form an SiX solution. Varnish solution V2 was prepared by mixing SiX solution (3g), Pd-785 stock solution ($3.10\text{E-}4\text{g}$, $3.94\text{E-}7\text{mol}$ in 0.1mL of methylene chloride), Rhodorsil 2074 stock solution ($1.60\text{E-}3\text{g}$, $1.58\text{E-}6\text{mol}$ in 0.1 mL of methylene chloride) and P2 copolymer solution (30g, solid 3g). The ratio of copolymer/monomers was 1/1 by weight and the ratio of monomers/Pd catalyst/Photo acid generator (PAG) was 25K/1/4 by mol. The varnish solution was filtered through a 0.2-micron pore filter.

Example V3

[0085] HxNB (42.03g, 0.24 mol) and SiX (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX 1076 (0.5g) and Ciba® IRGAFOS 168 (0.125g) to form a monomer-antioxidant solution. To 30.0g of copolymer solution (10g of P3 + 20g of P4), were added 3.0g of the monomer-antioxidant solution, Pd785 ($4.93\text{E-}4\text{g}$, $6.28\text{E-}7\text{mol}$ in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 ($2.55\text{E-}3\text{g}$, $2.51\text{E-}6\text{mol}$ in 0.1 mL of methylene chloride) to form the varnish solution V3. This solution was filtered through a 0.2-micron pore filter prior to use.

Example V4

[0086] Varnish Solution V4 was prepared as above for V3, except that the 30.0g of copolymer solution was 15g of P3 and 15g of P4 to form the varnish solution V4. This solution was filtered with 0.2-micron pore filter prior to use.

Example V5

[0087] Varnish Solution V5 was prepared as above for V3, except that the 30.0g of copolymer solution was 20g of P3 and 10g of P4 to form the varnish solution V5. This solution was filtered through a 0.2-micron pore filter prior to use.

Example V6

[0088] Varnish Solution V6 was prepared as above for V3, except that the 30.0g of copolymer solution was 30g of P3 to form the varnish solution V6. This solution was filtered through a 0.2-micron pore filter prior to use.

Example V7

[0089] HxNB (40.33g, 0.23 mol) and Norbornenylethyltriethoxysilane (TMSENB, CAS 68245-19-2) (9.67g, 0.039 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX 1076

(0.5g) and Ciba® IRGAFOS 168 (0.125g) to form a monomer-antioxidant solution. To 30.0g of the above copolymer solution (15g of P3 + 15g of P4) depicted in Table 1, were added 3.0g of the monomer-antioxidant solution, Pd785 (5.02E-4g, 6.39E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (2.59E-3g, 2.55E-6 mol in 0.1 mL of methylene chloride) to form the varnish solution V7. This solution was filtered through a 0.2-micron pore filter prior to use.

Example V8

[0090] HxNB (42.03g, 0.24 mol) and SiX, (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX 1076 (0.5g) and Ciba® IRGAFOS 168 (0.125g) to form a monomer-antioxidant solution. To 1.83g of the above prepared copolymer P5, were added 3.06g of the monomer-antioxidant solution, Pd785 (3.85E-4g, 4.91E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (1.99E-3g, 1.96E-6 mol in 0.1 mL of methylene chloride) and 1.30g of mesitylene and to form the varnish solution.

Example V9

[0091] HxNB (42.03g, 0.24 mol) and SiX, (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX 1076 (0.5g) and Ciba® IRGAFOS 168 (0.125g) to form a monomer-antioxidant solution. To 0.915g of the above prepared copolymer P6, were added 1.53g of the monomer-antioxidant solution, Pd785 (2.52E-4g, 3.21E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (1.30E-3g, 1.28E-6 mol in 0.1 mL of methylene chloride) and 0.645g of mesitylene to form the varnish solution.

Example V10

[0092] HxNB (42.03g, 0.24 mol) and SiX, (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX 1076 (0.5g) and Ciba® IRGAFOS 168 (0.125g) to form a monomer-antioxidant solution. To 2.0g of the above prepared copolymer P7, were added 2.4g of the monomer-antioxidant solution, Pd785 (3.95E-4g, 5.03E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (2.55E-3g, 2.51E-6 mol in 0.1 mL of methylene chloride) and 2.5g of toluene and to form the varnish solution. The varnish solution was filtered through a 0.2-micron pore filter prior to use.

Example V11

[0093] HxNB (42.03g, 0.24 mol) and SiX, (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX 1076 (0.5g) and Ciba® IRGAFOS 168 (0.125g) to form a monomer-antioxidant solution. To 2.0g of the above prepared homopolymer P8, were added 2.4g of the monomer-antioxidant solution, Pd785 (3.95E-4g, 5.03E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (2.55E-3g, 2.51E-6 mol in 0.1 mL of methylene chloride) and 6.12g of toluene to form the varnish solution. The varnish solution was filtered through a 5-micron pore filter prior to use.

Example V12

[0094] HxNB (42.03g, 0.24 mol) and (SiX) (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX® 1076 (0.5g) and Ciba® IRGAFOS® 168 (0.125g) to form a monomer-antioxidant solution. To 3.0g of the above prepared copolymer P9, were added 1.0g of the monomer-antioxidant solution, Pd(PCy3)2(OAc)2 (Pd785) (1.65E-4g, 2.10E-7mol in 0.1mL of methylene chloride), RHODORSIL® PHOTOINITIATOR 2074 (8.51E-4g, 8.38E-7 mol in 0.1 mL of methylene chloride) and 5.0g of toluene and to form the varnish solution.

Example V13

[0095] HxNB (42.03g, 0.24 mol) and (SiX) (7.97g, 0.026 mol) were weighed out into a glass vial. To this solution of monomers were added two antioxidants, Ciba® IRGANOX® 1076 (0.5g) and Ciba® IRGAFOS® 168 (0.125g) to form a monomer-antioxidant solution. To 3.0g of the above prepared copolymer P10, were added 2.0g of the monomer-antioxidant solution, Pd(PCy3)2(OAc)2 (Pd785) (3.29E-4g, 4.19E-7mol in 0.1mL of methylene chloride), TAG-372R photo acid generator (CAS 193957-54-9, available from Toyo Ink Mfg. Co., Ltd. Of Tokyo Japan) (7.63E-4g, 8.38E-6 mol in 0.1 mL of methylene chloride) and 10.0g of toluene to form the varnish solution.

[0096] Table 1 provides a summary of the composition of each varnish solution discussed above:

Table 1

	Polymer matrix / weight	Norbornene monomers			Pd-785		
		Mon 1 (mol %)	Mon 2 (mol %)	Wt.		PAG Wt./mol	R or T†
V1	P1 (3g)	HxNB (90)	SiX (10)	3g	4.94E-4g (6.29E-7mol)	2.55E-3g (6.29E-7mol)	R
V2	P2 (3g)	N/A	SiX (100)	3g	3.10E-4g (3.94E-7mol)	1.60E-3g (1.58E-6mol)	R
V3	P3 (1g) P4 (2g)	HxNB (90)	SiX (10)	3g	4.93E-4g (6.28E-7mol)	2.55E-3g (2.51E-6mol)	R
V4	P3 (1.5g) P4 (1.5g)	HxNB (90)	SiX (10)	3g	4.93E-4g (6.28E-7mol)	2.55E-3g (2.51E-6mol)	R
V5	P3 (2g) P4 (1.5g)	HxNB (90)	SiX (10)	3g	4.93E-4g (6.28E-7mol)	2.55E-3g (2.51E-6mol)	R
V6	P3 (3g)	HxNB (90)	SiX (10)	3g	4.93E-4g (6.28E-7mol)	2.55E-3g (2.51E-6mol)	R
V7	P3 (1.5g) P4 (1.5g)	HxNB (90)	TMSEN B (10)	3g	5.02E-4g (6.39E-7mol)	2.59E-3g (2.55E-6mol)	R
V8	P5 (1.8g)	HxNB (90)	SiX (10)	3.1g	3.85E-4g (4.91E-7mol)	1.99E-3g (1.96E-6mol)	R
V9	P6 (.92g)	HxNB (90)	SiX (10)	1.5g	2.52E-4g (3.21E-7mol)	1.30E-3g (1.28E-6mol)	R
V10	P7 (2g)	HxNB (90)	SiX (10)	2.4g	3.95E-4g (5.03E-7mol)	2.55E-3g (2.51E-6mol)	R
V11	P8 (2g)	HxNB (90)	SiX (10)	2.4g	3.95E-4g (5.03E-7mol)	2.55E-3g (2.51E-6mol)	R
V12	P9 (3g)	HxNB (90)	SiX (10)	1g	1.65E-4g (2.10E-7mol)	8.51E-4g (8.38E-7mol)	R
V13	P10 (3g)	HxNB (90)	SiX (10)	2g	3.29E-4g (4.19E-7mol)	7.63E-4g (8.38E-6mol)	T

† R indicates Rhodorsil 2074 was used and T indicates TAG-372R

Examples WG1-WG5

[0097] Examples WG1-WG5 demonstrate the fabrication of single-layer and three-layer waveguide structures in accordance with embodiments of the present invention. It will be noted that as each of the varnish solutions used in the exemplified methods, below, of forming waveguide structures incorporates a photo sensitive material, such structures were formed under yellow light.

Example WG1

Formation of a single-layer waveguide structure

[0098] The appropriate filtered varnish solution was poured onto a 4" glass wafer and spread to an essentially uniform thickness using a doctor blade. Then the coated glass wafer was placed on a vented leveling table overnight to allow the solvents to evaporate and form an essentially dry, solid film. The film was exposed

to UV light (365 nm) through a photomask (dose = 3000mJ) and then heated in an oven for 30 minutes at 85°C followed by heating for an additional 60 minutes at 150°C. A waveguide pattern was visible after the first heating step.

Example WG2

Formation of a three-layer waveguide structure

[0099] Varnish solution V8 was poured onto 250-micron thick PET film and spread to an essentially uniform thickness using a doctor blade (wet thickness = 70-micron). Then Varnish solution V9 was poured onto the first layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 80-micron). Finally the Varnish solution V8 was poured onto the second layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 80 micron). Then the coated PET film was placed on a hot plate and was heated at 50°C for 30minutes to allow the toluene to evaporate and form a solid accumulated film. The film was exposed to UV light (365nm) through a positive tone photomask (exposure dose = 3000mJ/cm²) and then placed on a hot plate for 30 minutes at 45°C followed by a cure for 30 minutes at 85°C and for 60 minutes at 150°C, respectively. A waveguide pattern was visible after the film was placed on a hot plate at 45°C for 10 minutes. Propagation loss for this waveguide was measured using a "cut back method" and was determined to be 6.0dB/cm.

Example WG3

Formation of a three-layer waveguide structure

[0100] The filtered Varnish solution V10 was poured onto 250-micron thick PET film and spread to an essentially uniform thickness using a doctor blade (wet thickness = 70-micron). Then filtered Varnish solution V11 was poured onto the first layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 80-micron). Finally the filtered Varnish solution V10 was poured onto the second layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 80-micron). Then the coated PET film was placed on a hot plate and was heated at 50°C for 45minutes to allow the toluene to evaporate and form a solid accumulated film. The film was exposed to UV light (365nm) through a positive tone photomask (exposure dose = 3000mJ/cm²) and then put in an oven for 30 minutes at 50°C followed by a cure for 30 minutes at 85°C and for 60 minutes at 150°C, respectively. A waveguide pattern was visible after the film was placed in an oven at 50°C for 10 minutes. Propagation loss for this waveguide was measured using a "cut back method" and was determined to be 3.0dB/cm.

Example WG4

Formation of a three-layer waveguide structure

[0101] The Varnish solution V13 was poured onto 250-micron thick PET film and spread to an essentially uniform thickness using a doctor blade (wet thickness = 70-micron). Then filtered Varnish solution V12 was poured onto the first layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 80-micron). Finally the Varnish solution V13 was poured onto the second layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 80-micron). Then the coated PET film was placed on a hot plate and was heated at 50°C for 45 minutes to allow the toluene to evaporate and form a solid accumulated film. The film was exposed to UV light (365nm) through a positive tone photomask (exposure dose = 3000mJ/cm²) and then put in an oven for 30 minutes at 50°C followed by a cure for 30 minutes at 85°C and for 60 minutes at 150°C, respectively. A waveguide pattern was visible after the film was placed in an oven at 50°C for 10 minutes.

Example WG5

Formation of a three-layer waveguide structure

[0102] Avatrel® 2000P solution (available from Promerus LLC, Brecksville, OH) was poured onto a 4" glass wafer and spread to an essentially uniform thickness using a spin coater (wet thickness = 1-micron). Then it was placed on a hot plate and heated at 100°C for 10 minutes and exposed to UV light without a photomask (exposure dose 400mJ/cm²) followed by curing at 110°C for 15 minutes and 160°C for 1 hour, respectively.

[0103] Then the varnish solution V14 was poured onto the surface of the cured Avatrel 2000P layer and spread to an essentially uniform thickness using a doctor blade (wet thickness = 70-micron). Then the coated glass wafer was placed on a vented leveling table overnight to allow the solvents to evaporate and form an essentially dry solid film. The following day the solid film formed of solution V14 was exposed to UV light (365nm) through a photomask (exposure dose 3000mJ/cm²) followed by aging at room temperature for 30 minutes, curing first at 85°C for 30 minutes and then at 150°C for 60 minutes. A waveguide pattern was visible after the film was cured at 85°C for 30 minutes.

[0104] Then a second portion of Avatrel 2000P solution was poured onto the surface of the cured layer of varnish solution V14 and spread to an essentially uniform thickness using a spin coater (wet thickness = 1 micron). The coated glass wafer was placed on a hot plate and heated at 100°C for 10 minutes and exposed to

UV light without a photomask (exposure dose 400mJ/cm²) followed by curing at 110°C for 15minutes and 160°C for 1hour, respectively. A waveguide pattern was still visible but the film looked brownish through the top cladding layer.

Propagation Loss Measurements

[0105] Propagation loss for each of the waveguides formed by five varnish solutions, V3-V7 was measured using a "cut back method." Each waveguide was a single-layer waveguide fabricated using the method of Example WG1. Light (830nm) generated from a LASER diode was input into a first end of the core of waveguide formed from each varnish solution through an optical fiber, where the waveguide had a first length. The power of the light output at an opposing, second end was measured. The waveguide was the "cut back" to at least two shorter lengths and the light output measured at the second output end for each length.

[0106] Total optical loss for each of the measurements is:

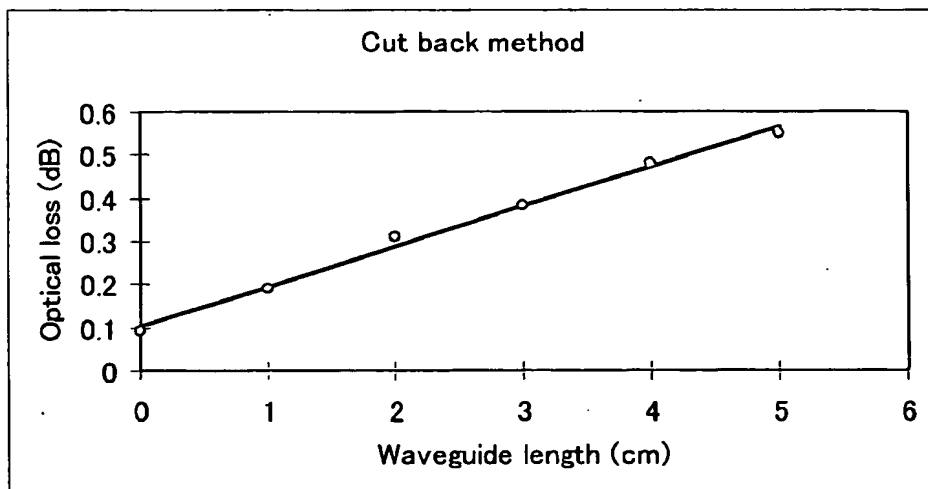
$$\text{Total Optical Loss (dB)} = -10\log(P_n/P_o)$$

where P_n is the measured output at the second end of the waveguide for each of the lengths P_1, P_2, \dots, P_n , and P_o is the measured output of the of the light source at the end of the optical fiber before such fiber is coupled to the first end of the waveguide core. The total optical loss is then plotted as exemplified in Chart 1 below. The resulting best straight line of this data is represented by the equation:

$$y = mx + b$$

where m is the propagation loss and b is the coupling loss.

Chart 1



[0107] Results of Propagation Loss using the "cut back" method for each of varnish solutions V3-V7 is presented in Table 2, below.

Table 2

Varnish solution #	V3	V4	V5	V6	V7
Propagation loss [dB/cm]	0.183	0.157	0.112	0.087	0.474

[0108] In addition to the examples of waveguide structures, and the materials used to form such structures discussed above, it is contemplated that varnish solutions can be prepared using a norbornene-type polymer where at least one of the repeat units of such polymer encompasses a pendant group having an epoxy moiety. An exemplary norbornene-type polymer is the copolymer of Hexyl Norbornene (HxNB) and Norbornenemethylglycidylether (AGENB) and an exemplary varnish solution would include such an HxNB/AGENB copolymer and an acid generator material for causing the epoxy moiety to open when desired. Such a varnish solution can have excellent adhesion to the films of the present invention that are used for forming waveguide channels and laterally adjacent cladding regions. Advantageously, in some envisioned embodiments, the acid generator material selected for such a varnish solution can be a photoinitiator such as RHORDORSIL 2074 or TAG-372R such that opening the epoxy moiety is contemporaneous with the forming of waveguide structures in an adjacent layer. In other embodiments the acid generator material can be selected to open the epoxy moiety in a manner independent of the forming of waveguide structures in the adjacent layer. For example, an acid generator material can be selected that is not absorbing at the same wavelengths as the photoinitiator used in the waveguide forming layer or that is thermally activated rather than photonically activated. In another variation, a nonabsorbing photobase generator (PBG) or a thermal base generator (TBG) can be used in the varnish solution. This will provide another route to the ring opening of the epoxy functional groups.

[0109] Thus it is envisioned that three-layer waveguide structures can be made in accordance with embodiments of the present invention using varnish solutions encompassing polymers with norbornene-type repeat units that include an epoxy moiety. For example, referring to Fig. 9, layers 110 and 130 can be formed using such polymers having norbornene-type repeat units that include an epoxy moiety.

CLAIMS:

1. A photo-induced thermally developable film comprising:
a polymer matrix comprising one or more norbornene-type repeat units;
at least one norbornene-type monomer;
a procatalyst; and
a photoinitiator.
2. The film of Claim 1 further comprising at least one antioxidant.
3. The film of Claim 2 where the polymer matrix is a homopolymer or copolymer of norbornene-type monomers.
4. The film of Claim 3 where the polymer matrix is a copolymer.
5. The copolymer of Claim 4 where said copolymer comprises hexyl norbornene repeat units and diphenylmethyl norbornenemethoxy silane repeat units.
6. The film of Claim 1 where the at least one norbornene-type monomer comprises a norbornene-type crosslinker monomer.
7. The film of Claim 6 further comprising at least one antioxidant.
8. The film of Claim 7 where the at least one norbornene-type monomer further comprises a norbornene-type monomer having an alkyl pendant group.
9. The film of Claim 1 further comprising at least one antioxidant and where the at least one norbornene-type monomer comprises hexyl norbornene and bis-norbornenemethoxy dimethylsilane.
10. The film of Claim 1 where the polymer matrix is a copolymer comprising hexyl norbornene repeat units and diphenylmethyl norbornenemethoxy silane repeat units; the at least one norbornene-type monomer comprises hexyl norbornene and bis-norbornenemethoxy dimethylsilane and the film further comprises an antioxidant.

11. An optical wave guide comprising a waveguide layer comprising a core region and laterally adjacent cladding regions, wherein the waveguide layer comprises a first norbornene-type polymer material.

12. The optical wave guide of Claim 11, wherein the first norbornene-type polymer material is a copolymer comprising two different types of norbornene-type repeating units.

13. The optical wave guide of Claim 11 further comprising a cladding layer adjacent the waveguide layer wherein the laterally adjacent cladding regions and the cladding layer collectively surround the core region, and where the cladding layer comprises a second norbornene-type polymer material.

14. The optical wave guide of Claim 13, where the first norbornene-type polymer material comprises hexyl norbornene repeating units.

15. The optical wave guide of Claim 14, where the second norbornene-type polymer material comprises hexyl norbornene repeating units.

16. The optical wave guide of Claim 14, where the second norbornene-type polymer material comprises norbornene-type repeating units that include a pendant group having an epoxy moiety.

17. A method of forming an optical wave guide structure comprising:
providing a first material layer comprising a norbornene-type polymer matrix and a photo acid generator, a procatalyst and a norbornene-type monomer dispersed uniformly in the norbornene-type polymer matrix, the first material layer having a first refractive index (RI);

causing the photo acid generator to generate an acid and a weakly coordinating anion (WCA) in a predetermined region of the first material layer, the acid and WCA serving to convert at least some of the procatalyst within the predetermined region to an active but latent catalyst; and

activating the active but latent catalyst to cause polymerization of the norbornene-type monomer in the predetermined region, where the polymerization causes the first RI to become a second RI within the predetermined area and a third RI in a region laterally adjacent the predetermined region, where one of the predetermined region and the laterally adjacent region is a waveguide core region and the other is a waveguide clad region, the waveguide core region and laterally adjacent waveguide clad region being optical waveguide structures.

18. The method of Claim 17, further comprising providing a second material layer disposed on the first material layer, where the second material layer comprises a norbornene-type polymer.

19. The method of Claim 18, where the norbornene-type polymer of the second material layer comprises a norbornene-type repeating unit having a pendant group comprising an epoxy moiety.

20. The method of Claim 17, further comprising after the activating, heating the first material layer to a first temperature for a first period of time and subsequently heating the first material layer to a second temperature for a second period of time, where the second temperature is higher than the first temperature.

ABSTRACT OF THE DISCLOSURE

Embodiments in accordance with the present invention provide waveguide structures encompassing norbornene-type polymers and methods of forming such structures where core and laterally adjacent cladding regions are photonically defined. Some embodiments of the present invention provide waveguide structures where core regions are collectively surrounded by laterally adjacent cladding regions and cladding layers that encompass norbornene-type polymers and methods of forming such structures.

FIG. 1

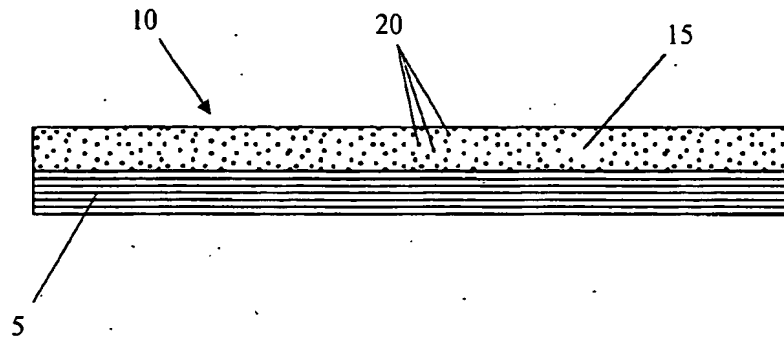


FIG. 2

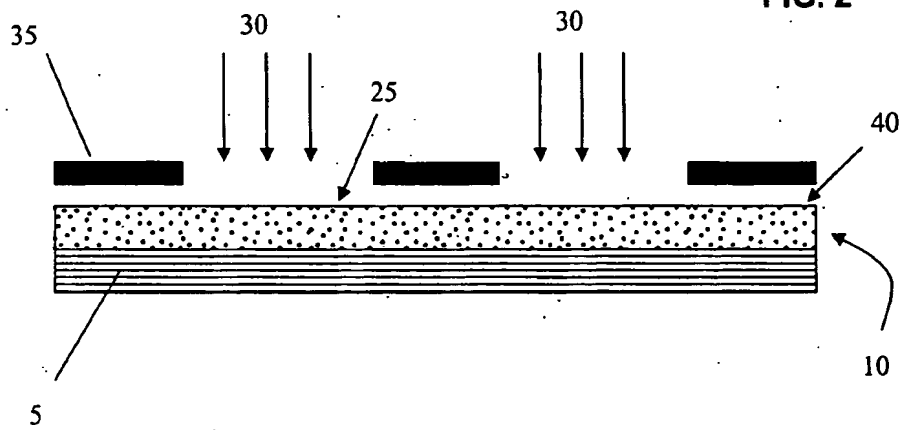
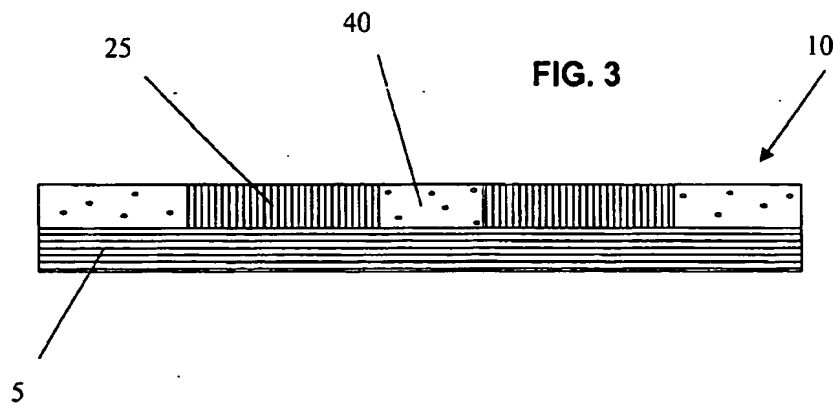


FIG. 3



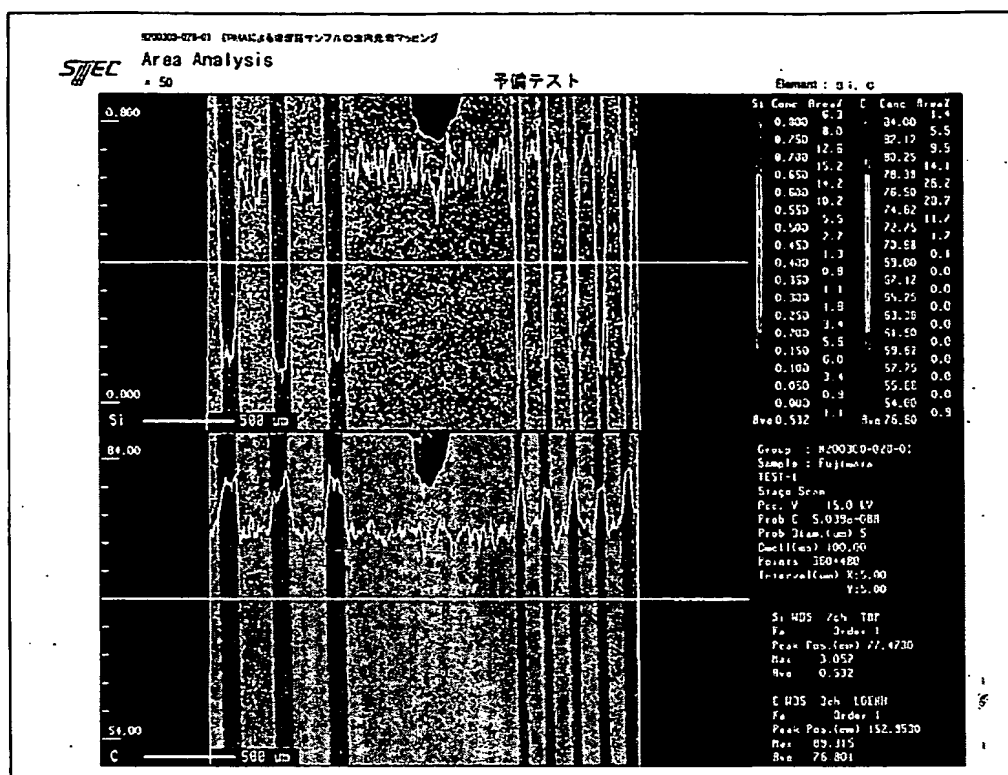


Fig. 4

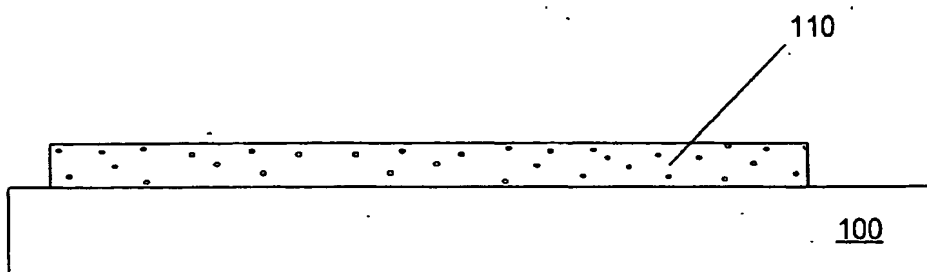


FIG. 5

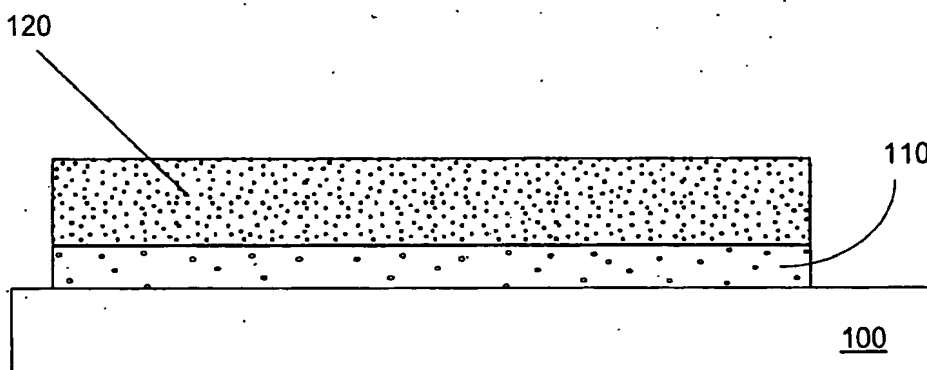


FIG. 6

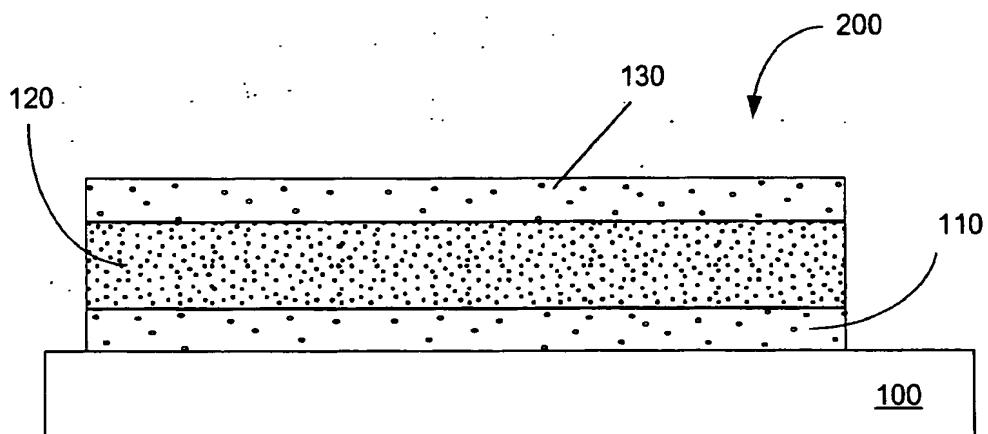


FIG. 7

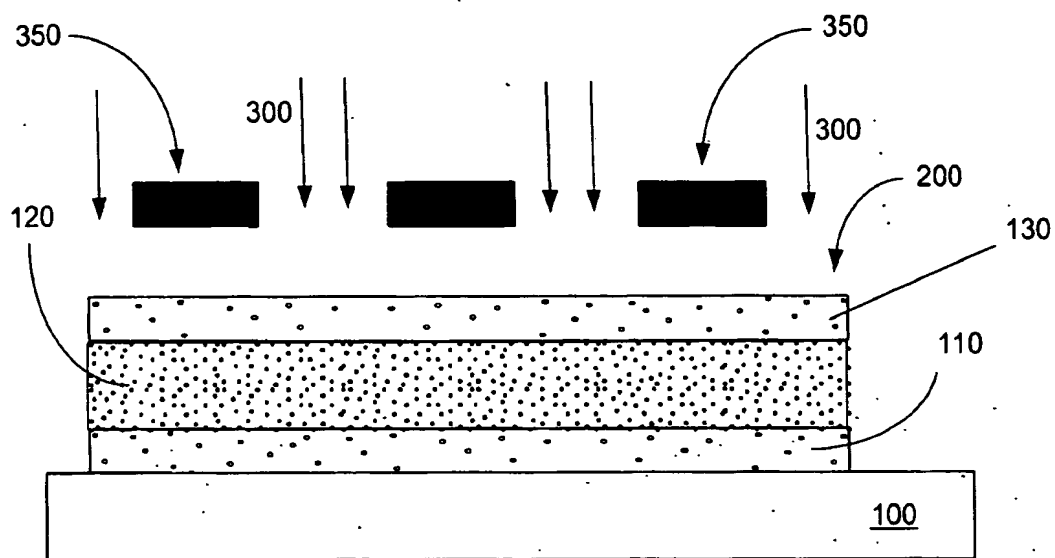


FIG. 8

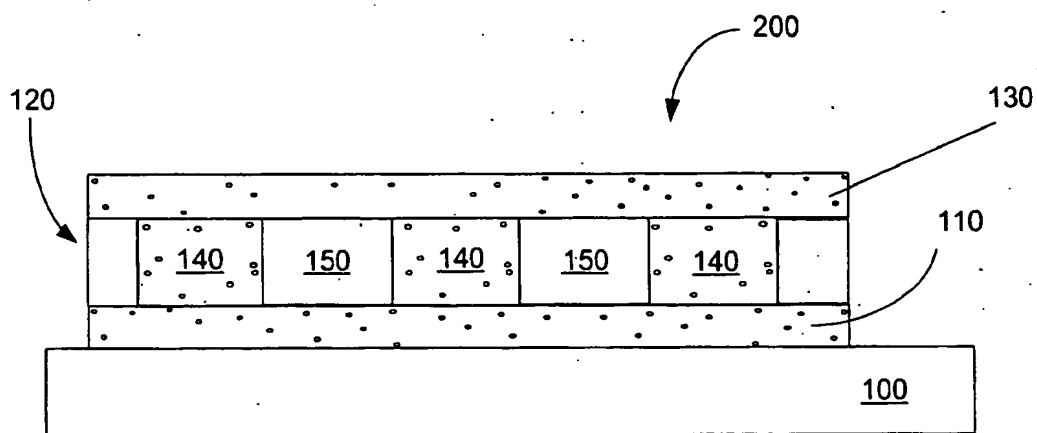
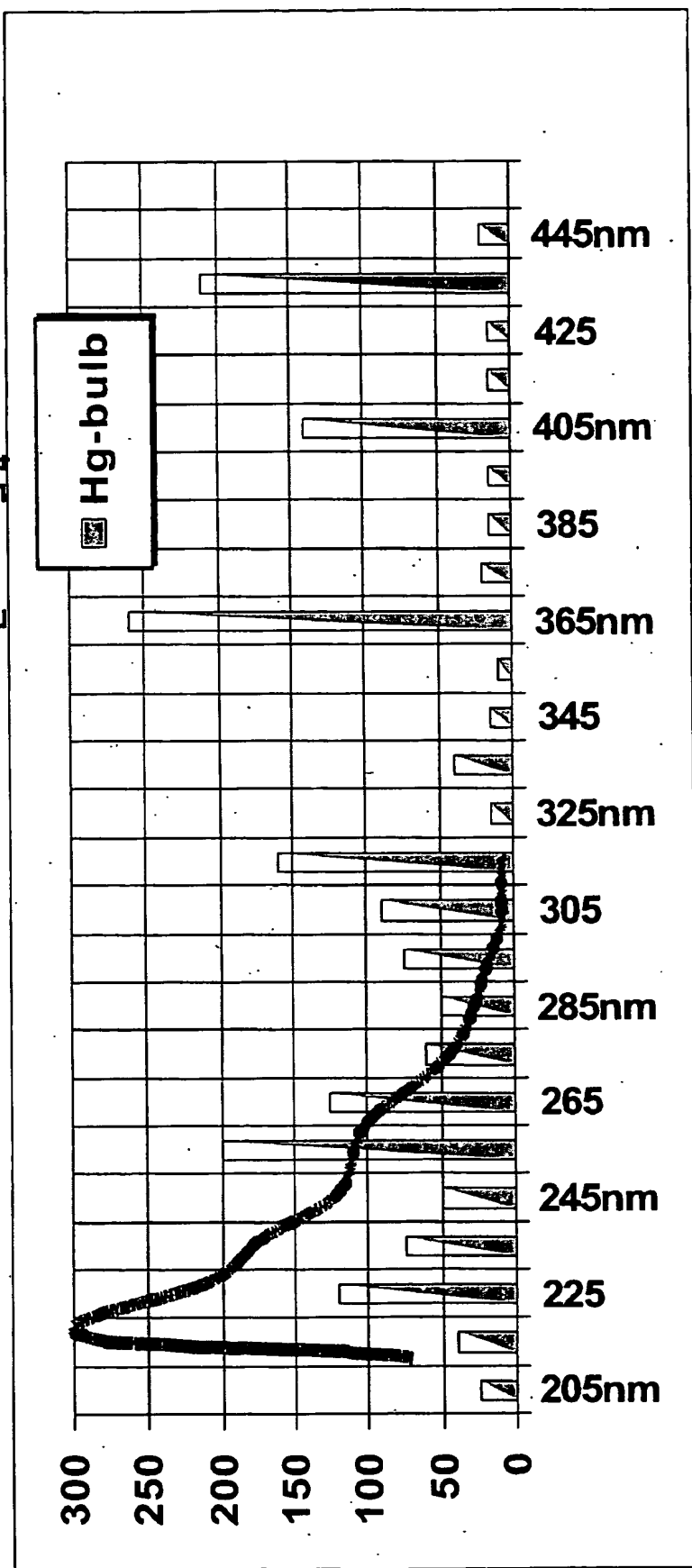
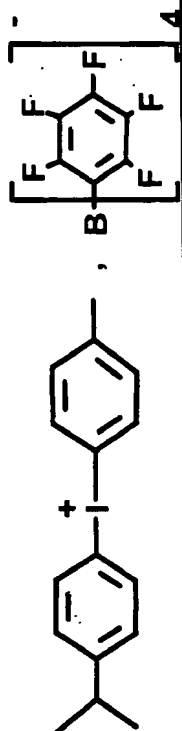


FIG. 9

Fig. 10



Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/037188

International filing date: 22 November 2004 (22.11.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/523,978
Filing date: 21 November 2003 (21.11.2003)

Date of receipt at the International Bureau: 22 December 2004 (22.12.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record.

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:



☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**



☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**



☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.